Macromolecules **1994,** *27,* 4787-4794 **4787**

Quantum Yield of Photosensitized Singlet Oxygen ($a^1\Delta_g$) Production in Solid Polystyrene

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Received April 7, 1994; Revised Manuscript Received June 1, 1994[®]

ABSTRACT: The quantum yield of singlet oxygen ($a^1\Delta_g$), produced by energy transfer from the photosensitizer acridine, has been determined by two independent spectroscopic methods in solid polystyrene. Upon 355-nm pulsed-laser irradiation of acridine at 1.3 mJ/pulse, the $O_2(a^1\Delta_g)$ quantum yield in polystyrene [ϕ_Δ^{PS}(acridine) = 0.56 ± 0.05] is slightly smaller than that in a liquid solvent analog such as benzene [ϕ_Δ^{benz}(acridine) = 0.83 ± 0.06]. These data indicate that the photosensitized yields of $O_2(a^1\Delta_g)$ in a solid polymer matrix can nevertheless be appreciable, which may be important for understanding the photodegradation of some polymeric materials or of dyes and other additives dissolved in those materials.

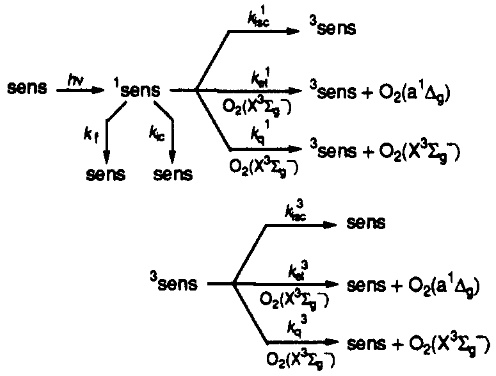
Introduction

The lowest excited electronic state of molecular oxygen, singlet oxygen ($a^1\Delta_g$), can be produced in solid organic polymers and liquid solvents by several methods, of which photosensitization is the most common.[1,2] In this method, $O_2(a^1\Delta_g)$ is formed by the transfer of energy from an excited-state donor molecule (i.e., a sensitizer) to ground-state oxygen ($X^3\Sigma_g^-$). The excited-state sensitizer is created by photolysis at wavelengths that, depending on the sensitizer, can range from the UV to near-IR. The list of molecules that can act as a $O_2(a^1\Delta_g)$ sensitizer is extensive, as documented in a recent compilation of solution-phase data.[3]

$O_2(a^1\Delta_g)$ is an acknowledged intermediate in the photo-induced and radiation-induced oxygenation reactions of many organic compounds, including some polymeric systems.[4-6] Thus, upon exposure to light, aerated macromolecular materials, and low molecular weight compounds dissolved in these materials, may degrade by a mechanism that involves $O_2(a^1\Delta_g)$. Attempts to understand events that result both in the formation and removal of $O_2(a^1\Delta_g)$ are consequently of interest from a practical as well as fundamental perspective.[7-12]

In a photosensitized process, $O_2(a^1\Delta_g)$ is most often produced by the sensitizer triplet state. Although $O_2(a^1\Delta_g)$ yields are sensitizer dependent, the triplet-state energy of most organic molecules nevertheless exceeds the required 22.5 kcal/mol, which is the $O_2(a^1\Delta_g)$ excitation energy. Furthermore, triplet-state lifetimes are almost always long enough that quenching by $O_2(X^3\Sigma_g^-)$ is efficient in both liquids and solid polymers. The shorter-lived sensitizer singlet state can also act as a $O_2(a^1\Delta_g)$ precursor. In this case, however, the effects of a smaller oxygen diffusion coefficient in the polymer are pronounced, and the efficiency of singlet state quenching by oxygen in the solid medium is much less than that in liquid solvents. For example, with a molecule whose singlet state lifetime is ~10 ns, we can calculate that more than 50% of the singlet states will typically be quenched by $O_2(X^3\Sigma_g^-)$ in an oxygen-saturated liquid solution, whereas less than 2% will be quenched in solid polystyrene.[13] Because oxygen-induced deactivation of the excited-state singlet usually yields the triplet state, this phenomenon can have a large effect on the overall $O_2(a^1\Delta_g)$ yield. Events that result in the photosensitized production of $O_2(a^1\Delta_g)$ are depicted in Scheme 1. [Superscripts denote spin multiplicity and subscripts denote fluorescence (f), intersystem crossing (isc), internal conversion (ic), energy transfer (et), and quenching (q)].

Scheme 1



In the comparatively simple case where the energy difference between ¹sens and ³sens is less than 22.5 kcal/mol and $O_2(a^1\Delta_g)$ is produced only by the sensitizer triplet state (i.e., $k_{et}^1 = 0$), the $O_2(a^1\Delta_g)$ quantum yield ϕ_Δ will depend on (a) the triplet state yield ϕ_T, (b) the fraction F_{oxy}^T of triplet states quenched by oxygen, and (c) the fraction f_Δ^T of these oxygen quenching reactions that yield $O_2(a^1\Delta_g)$. These important parameters are expressed below in terms of processes shown in Scheme 1:

$$\phi_T \propto \frac{k_{isc}^1 + k_q^1[O_2(X^3\Sigma_g^-)]}{k_f + k_{ic} + k_{isc}^1 + k_q^1[O_2(X^3\Sigma_g^-)]} \tag{1a}$$

$$F_{oxy}^T = \frac{(k_{et}^3 + k_q^3)[O_2(X^3\Sigma_g^-)]}{k_{isc}^3 + (k_{et}^3 + k_q^3)[O_2(X^3\Sigma_g^-)]} \tag{1b}$$

$$f_\Delta^T = \frac{k_{et}^3}{k_{et}^3 + k_q^3} \tag{1c}$$

Certainly, the large decrease in solute diffusion coefficients that accompanies the change from a liquid to solid solvent

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® Abstract published in *Advance ACS Abstracts,* July 15, 1994.

0024-9297/94/2227-4787$04.50/0

system can affect bimolecular quenching rate constants, and thereby influence ϕ_Δ. Furthermore, it is possible that solvent cage effects, unique to the more rigid polymer, may affect ϕ_Δ by changing f_Δ^T (e.g., the sensitizer itself may quench $O_2(a^1\Delta_g)$ once it is formed).

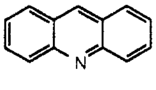
In our previous work,[1,14-16] we found that the behavior of $O_2(a^1\Delta_g)$, as manifested in a variety of photophysical and photochemical processes, can indeed be significantly different in solid polymers as compared to liquid solvents. This phenomenon can have important ramifications, particularly if a solution-phase perspective is used to evaluate the $O_2(a^1\Delta_g)$-mediated degradation of a solid polymer. Nevertheless, it is encouraging to note that a data base of important parameters that characterize the behavior of $O_2(a^1\Delta_g)$ in solid polymers is slowly developing. Despite extensive studies, however, both by ourselves and other investigators,[1,14-25] there has never been, to our knowledge, a systematic determination of the photosensitized $O_2(a^1\Delta_g)$ quantum yield ϕ_Δ in a solid macromolecular matrix.

In 1984, Krasnovskii and co-workers[20] reported that the quantum yield of chlorophyll-sensitized $O_2(a^1\Delta_g)$ phosphorescence was ~2–3 times smaller in a polystyrene film than in an acetone solution. The phosphorescence yield ϕ_P is equal to the $O_2(a^1\Delta_g)$ quantum yield ϕ_Δ multiplied by the fraction of $O_2(a^1\Delta_g)$ molecules that radiatively decay (eq 2).

$$\phi_P = \phi_\Delta k_r \tau_\Delta \qquad (2)$$

The fraction of $O_2(a^1\Delta_g)$ that radiatively decays is conveniently expressed as the product of the radiative rate constant (k_r) for $O_2(a^1\Delta_g)$ decay and the overall lifetime τ_Δ of $O_2(a^1\Delta_g)$, both of which are solvent dependent.[26] When we normalize the Krasnovskii et al. ϕ_P data for solvent dependent changes in k_r and τ_Δ, their results indicate that the chlorophyll-sensitized $O_2(a^1\Delta_g)$ quantum yield is ~5 times greater in acetone than in polystyrene. In a similar comparison of porphyrin-sensitized $O_2(a^1\Delta_g)$ phosphorescence intensities, Byteva et al.[22] report that ϕ_P in a polyester film is $\sim 2 \times 10^3$ times smaller than in a CCl_4 solution. Byteva et al. suggest that this large difference in ϕ_P values is due principally to an equally large difference in ϕ_Δ values. Because ϕ_P and ϕ_Δ depend on several terms that can vary significantly as the solvent is changed from a liquid to a solid polymer (*vide supra*), the results of Krasnovskii et al. and Byteva et al. could derive from a variety of phenomena.

In an attempt to better understand events that can influence values of ϕ_Δ in bulk polymers, it is first necessary to systematically quantify absolute yields for the sensitized production of $O_2(a^1\Delta_g)$ in a solid organic polymer and to compare these data to those recorded in an analogous liquid solvent. Acridine has been extensively studied as a $O_2(a^1\Delta_g)$ photosensitizer in liquid solutions and is now recommended as a standard for comparative measurements of $O_2(a^1\Delta_g)$ yields.[3] Acridine has several features that make it a useful $O_2(a^1\Delta_g)$ photosensitizer:[27,28] (1) It has an excited-state singlet lifetime short enough to preclude quenching by oxygen. Thus, ^{1}acridine is not a precursor to $O_2(a^1\Delta_g)$. (2) The precursor to $O_2(a^1\Delta_g)$, the acridine triplet state, is formed rapidly [<17 ps in benzene] and efficiently [ϕ_{isc}(benzene) = 0.84] from the singlet state. (3) The fraction f_Δ^T of acridine triplet states quenched by $O_2(X^3\Sigma_g^-)$ which yields $O_2a^1\Delta_g)$ is unity.[3,27] And (4) acridine is stable both upon prolonged photolysis in a hydrocarbon solvent and under free radical polymerization conditions.



Acridine

We report herein the results of two independent spectroscopic measurements in which the acridine-sensitized quantum yield of $O_2(a^1\Delta_g)$ was determined in bulk solid polystyrene (PS). The data are compared to the $O_2(a^1\Delta_g)$ quantum yield determined in a liquid analog (toluene).

Experimental Section

A. Instrumentation. The apparatus used is shown in Figure 1. The 1270-nm phosphorescence of $O_2(a^1\Delta_g)$ was monitored in a time-resolved experiment. Both the $O_2(a^1\Delta_g)$ sensitizer and the $O_2(a^1\Delta_g)$ chemical trap (rubrene) were monitored in time-resolved absorption experiments. The instrument was configured such that it was possible to perform both the flash absorption and phosphorescence experiments simultaneously. Our standard flash absorption apparatus[1,14,29] was modified in order to render the pulsed photolysis beam and continuous-wave absorption probe beam collinear at the sample (S) under study. The probe source was a 150-W xenon lamp (Osram). The probe beam was collimated so that it passed through the sample with a homogeneous cross section defined by an aperture (A1) placed immediately in front of the sample. The aperture was 1.00 cm in diameter, giving a probe beam cross-sectional area of 0.785 cm^2. The sample was protected from the intense and broad spectral output of the probe beam by (a) a Schott cutoff filter F (GG435 for measurements at 440 nm, GG515 for measurements at 530 nm), and (b) a Vincent Associates, Inc. "UniBlitz" shutter (Sh) that remained open for only 60 ms during each measurement.

The photolysis beam was the third harmonic (355 nm) of a Nd:YAG laser with a pulse duration of approximately 5 ns (FWHM), and a Gaussian cross-sectional intensity profile. Experiments were performed with photolysis energies that did not exceed 2.0 mJ/pulse. The photolysis beam was made to overlap with the probe beam by using a quartz plate beam splitter (BS). The diameter of the laser beam was restricted to 5 mm with an aperture (A2) so that it passed unclipped through the probe beam aperture A1. This ensured that the entire excitation beam passed through the probed volume of the sample. A portion of the laser excitation beam passed through the beam splitter to an energy meter (Scientech model 38-1UV5). The energy meter calibration provided by the manufacturer was confirmed by using the potassium ferrioxalate actinometer.[30] The beam-splitter factor (% reflected/% passed) was measured so that we were able to determine the energy of each laser pulse arriving at the sample.

The probe beam was focused into a monochromator set to pass (a) 530 nm when rubrene photobleaching was monitored, and (b) 440 nm when the acridine triplet state was monitored. The probe spectral resolution was approximately ±5 nm. The probe detector was an RCA 931-A photomultiplier tube (PMT) configured to use only eight amplification stages. The response of the flash absorption detection system was single exponential with a time constant of 90 ns. The PMT output was processed by using a Tektronix model 7912 waveform digitizer interfaced to an IBM personal computer.

A 5-mm diameter Ge detector (Germanium Power Devices Corporation) was used to monitor $O_2(a^1\Delta_g)$ phosphorescence. The 25 °C element was not biased. The photoinduced voltage drop across a 100-Ω load resistor was amplified and digitized by a Biomation model 8100 waveform recorder. The response of the $O_2(a^1\Delta_g)$ detection system was single exponential with a time constant of 2 μs.

The $O_2(a^1\Delta_g)$ phosphorescence signal was isolated with an interference filter (Barr Associates) centered at 1270 nm whose band pass at half-maximum was 80 nm. This filter was placed between two lenses (*f*-number = 0.85 and 1.0, respectively). In the chemical trapping experiments (method 1, *vide infra*), a spherical mirror (M) was placed opposite the sample from the detector. These optics enhanced the $O_2(a^1\Delta_g)$ signal intensity 5-fold compared to data recorded when the detector and

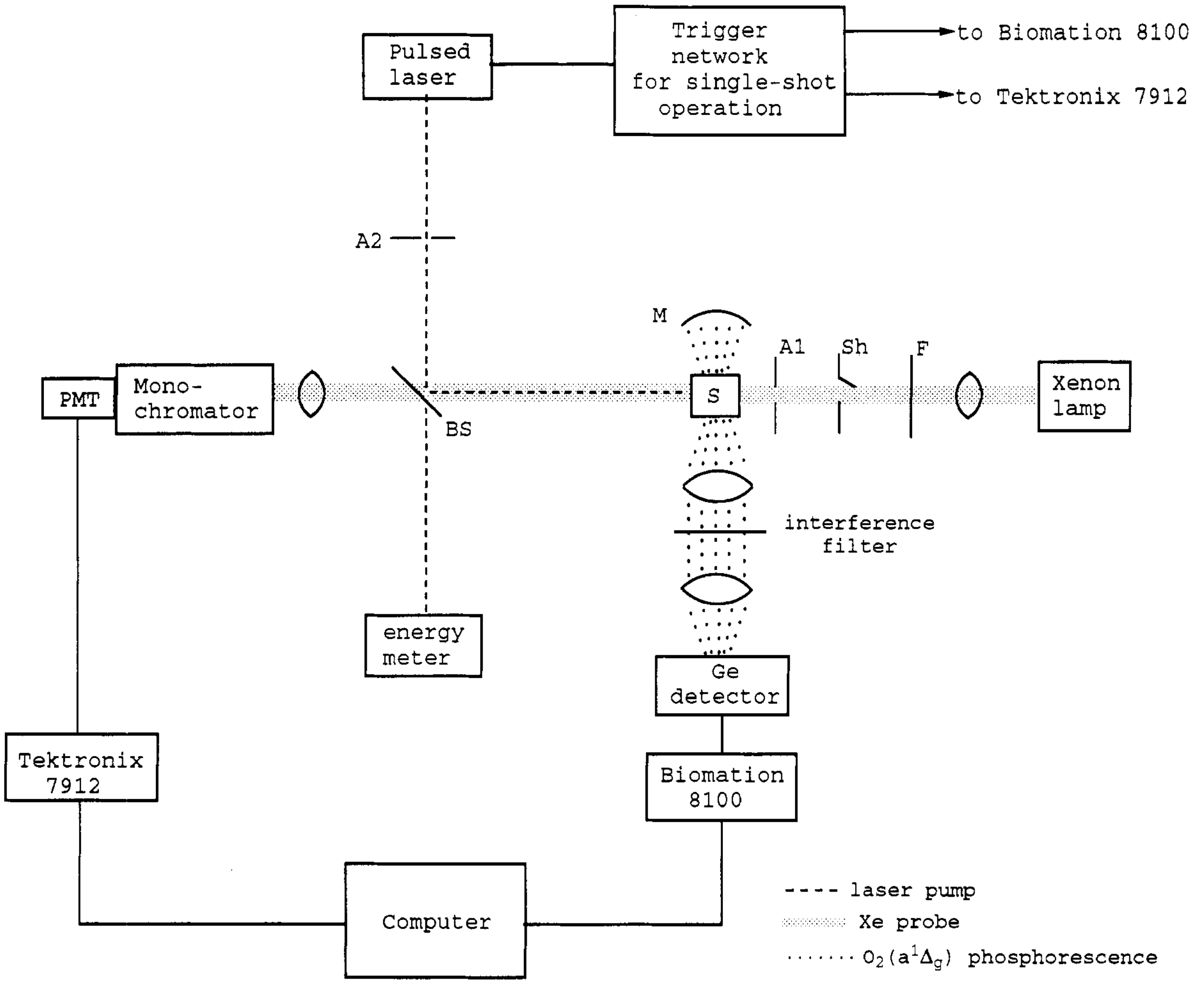


Figure 1. Schematic diagram of the experimental apparatus: A1 and A2, apertures; Sh, shutter; F, filter; BS, beam splitter; M, mirror; S, sample; PMT, photomultiplier tube.

interference filter were close-coupled to the sample. This mirror was not used in the phosphorescence intensity measurements (method 2) in order to more easily correct the detected phosphorescence intensity for changes in the solvent refractive index.

A home-built, manually operated pulse generator was used to trigger the laser and digitizers for "single-shot" operation. Polymer samples were subjected to only four photolysis pulses prior to disposal. Data from each laser shot were analyzed independently.

Absorption spectra were recorded on a Beckman DU-40 UV-vis spectrophotometer.

B. Sample Preparation. Acridine (Aldrich) was recrystallized twice from ethanol/water. Rubrene (Aldrich) was recrystallized from benzene under red light. Mesoporphyrin IX dimethyl ester (MP9) from Porphyrin Products was used as received. Rose bengal ethyl ester tetrabutylammonium salt (RB) was prepared as described elsewhere.[31,32] 1,3-Diphenylisobenzofuran (Aldrich) was recrystallized from a benzene/ethanol mixture under dim lighting. All polystyrene samples were prepared by free-radical polymerization of styrene as previously described.[14] Toluene (Aldrich HPLC grade) was used as received.

The samples used to determine ϕ_Δ by comparing $O_2(a^1\Delta_g)$ phosphorescence intensities were cut and polished[14] to the same dimensions of the fluorimeter cuvettes used for the liquid samples (1 cm × 1 cm).

The samples used to determine ϕ_Δ by chemical trapping were 1-mm thick and contained either (a) acridine at $\sim 1.0 \times 10^{-3}$ M or (b) acridine and rubrene at $\sim 1.0 \times 10^{-3}$ and $\sim 8.0 \times 10^{-4}$ M, respectively. In these samples, the acridine absorbance at 355 nm (~ 0.7) and rubrene absorbance at 530 nm (~ 0.6) were obtained by subtracting the small "apparent absorbance" due to light scattering from polystyrene (see Figure 2). These samples were cut and polished under red light. Measurements were made either (a) after O_2 saturation for 1 day at 80 psi or (b) after air equilibration for 3 days. Polymer samples used for the measurement of τ_T(acridine) and τ_T(RB) in the absence of oxygen were cut and polished under an atmosphere of nitrogen, and sealed in an oxygen-free chamber for data collection.

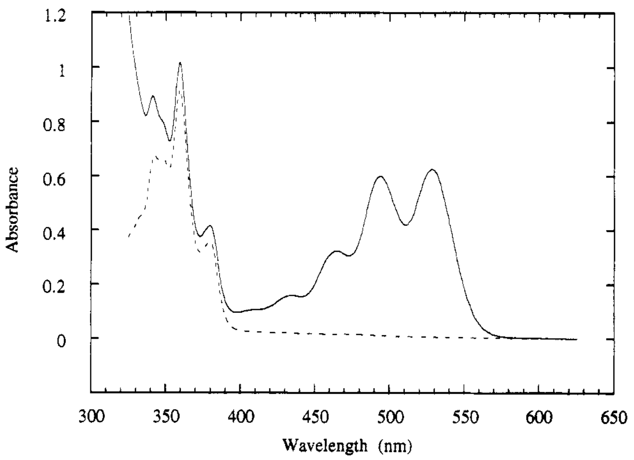


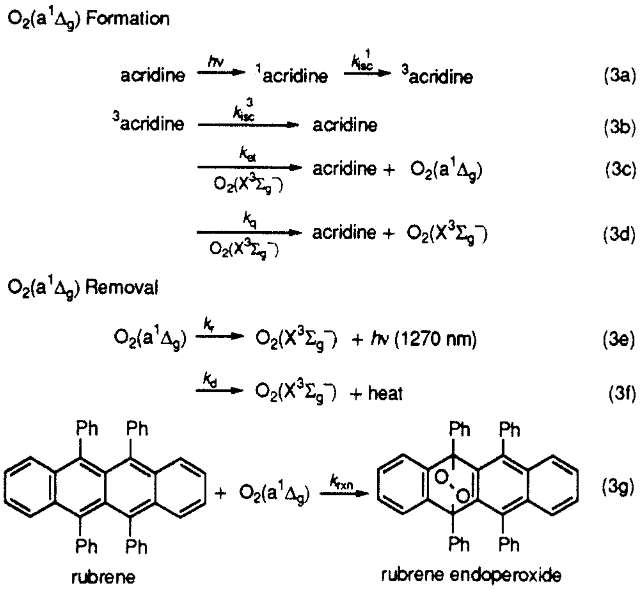
Figure 2. Absorption spectra recorded from 1-mm-thick polystyrene samples that contain (a) 1×10^{-3} M acridine (- - -), and (b) 1×10^{-3} M acridine and 8×10^{-4} M rubrene (—).

Results

The quantum yield of $O_2(a^1\Delta_g)$ production by acridine in solid polystyrene [ϕ_Δ^{PS}(acridine)] was determined by two independent methods.

Method 1. Chemical Trapping of $O_2(a^1\Delta_g)$. Description of the Method. In this approach to determine ϕ_Δ(acridine), the number of photons absorbed by acridine,

Scheme 2



and the resultant amount of $O_2(a^1\Delta_g)$ formed, were independently measured. The amount of light arriving at the sample was quantified by using a calibrated energy meter, and the moles of photons subsequently absorbed were calculated from the sample absorbance.

A reaction in which $O_2(a^1\Delta_g)$ was chemically trapped was used to quantify the amount of $O_2(a^1\Delta_g)$ formed. Rubrene (5,6,11,12-tetraphenylnaphthacene) was selected as the $O_2(a^1\Delta_g)$ trapping agent for the following reasons: (a) It is stable under the free-radical polymerization conditions through which the polystyrene samples were prepared. (b) It efficiently removes $O_2(a^1\Delta_g)$ [$k^{TOL} = (4.5 \pm 0.3) \times 10^7$ M^{-1} s^{-1}; $k^{PS} = (1.60 \pm 0.15) \times 10^7$ M^{-1} s^{-1}].[33] (c) It appears that rubrene does not promote the *physical* deactivation of $O_2(a^1\Delta_g)$ to $O_2(X^3\Sigma_g^-)$. By using the comparative technique of Trozzolo et al.[36] in which the $O_2(a^1\Delta_g)$-mediated removal of 1,3-diphenylisobenzofuran served as a standard, we determined that the rate constant for the *reaction* of $O_2(a^1\Delta_g)$ with rubrene in toluene [$(4.8 \pm 0.9) \times 10^7$ M^{-1} s^{-1}] is identical to the *overall* rate constant for $O_2(a^1\Delta_g)$ removal independently obtained from $O_2(a^1\Delta_g)$ lifetime studies (*vide supra*). (d) The product formed upon $O_2(a^1\Delta_g)$ removal, rubrene endoperoxide, is stable under the reaction conditions. And (e) rubrene can be spectroscopically monitored at 530 nm, where neither acridine nor the rubrene endoperoxide absorbs (Figure 2). [Although rubrene can also sensitize the production of $O_2(a^1\Delta_g)$, the 530-nm probe used to monitor the disappearance of rubrene under our conditions did not itself promote the bleaching of rubrene during the measurement period.] Events pertinent to the formation and removal of $O_2(a^1\Delta_g)$ in this system are depicted in Scheme 2. Once formed, $O_2(a^1\Delta_g)$ will be removed from the system by a variety of competing channels. Only a fraction of the $O_2(a^1\Delta_g)$ present in the system will encounter rubrene. We assume that in solid polystyrene, like toluene, rubrene quenching of $O_2(a^1\Delta_g)$ results only in endoperoxide formation (eq 3g), and that the rubrene-induced physical deactivation of $O_2(a^1\Delta_g)$ to $O_2(X^3\Sigma_g^-)$ is comparatively slow. This assumption is discussed further in the next section. Thus, in a given laser pulse, the amount of rubrene consumed is equal to the amount of $O_2(a^1\Delta_g)$ formed multiplied by the fraction F of $O_2(a^1\Delta_g)$ that reacts with rubrene (eq 4). For comparatively small changes in the rubrene concentration, F can be expressed in terms of the initial rubrene concentration:

$$\delta[\text{rubrene}] = [O_2(a^1\Delta_g)]F \tag{4}$$

$$F = \frac{k_{rxn}[\text{rubrene}]}{k_r + k_d + k_{rxn}[\text{rubrene}]} \tag{5a}$$

F can also be represented as 1 minus the fraction of $O_2(a^1\Delta_g)$ that decays by nonreactive paths (eq 5b), which is con-

$$F = 1 - \frac{k_r + k_d}{k_r + k_d + k_{rxn}[\text{rubrene}]} = 1 - \frac{\tau_\Delta}{\tau_\Delta^0} \tag{5b}$$

venient because ($k_r + k_d$) and ($k_r + k_d + k_{rxn}$[rubrene]) are the reciprocals of the easily-measured $O_2(a^1\Delta_g)$ lifetimes in the absence (τ_Δ^0) and presence (τ_Δ) of rubrene, respectively.

The change in rubrene concentration was quantified by using the Beer–Lambert law and monitoring the change in absorbance A of the band centered at ~530 nm (eq 6).[37]

$$\delta[\text{rubrene}] = \frac{\delta A_{530}}{\epsilon_{530}\ell} \tag{6}$$

The moles of rubrene consumed can be calculated using (eq.7):

$$\delta\text{moles} = \delta[\text{rubrene}]\pi r^2 \ell \tag{7}$$

where the volume of monitored rubrene is determined by the probe beam radius (r = 0.050 dm) and the sample thickness (ℓ = 0.01 dm).

Rubrene also has a small absorbance at the photolysis wavelength of 355 nm. Thus, in priniciple, our experiment could be flawed because rubrene could self-sensitize its own photooxygenation. At the concentrations of rubrene and acridine used in our experiments, however, only 5% of the incident radiation at 355 nm is absorbed by rubrene (see Figure 2). Furthermore, the combination of a short rubrene singlet-state lifetime (16 ns),[38] a high quantum efficiency of rubrene fluorescence ($\phi \approx 1$),[38] and the comparatively small oxygen diffusion coefficient in solid polystyrene, minimizes the rubrene-sensitized production of $O_2(a^1\Delta_g)$ under our conditions. Indeed, at [rubrene] $\approx 8 \times 10^{-4}$ M, we have found that the quantum yield of rubrene self-sensitized photooxygenation in solid polystyrene is <0.05.[31,35,39] Thus, an accurate measure of the number of incident photons that result in $O_2(a^1\Delta_g)$ production can be obtained by treating rubrene as a benign internal filter in a solution of the photosensitizer acridine.

The Measurements. On the basis of the preceding material, the quantum yield of $O_2(a^1\Delta_g)$ can be expressed as

$$\phi_\Delta(\text{acridine}) = \frac{\delta A_{530}\pi r^2}{\epsilon_{530}[1 - (\tau_\Delta/\tau_\Delta^0)]}(\text{moles of photons absorbed})^{-1} \tag{8}$$

Thus, the following measurements provide the amount of $O_2(a^1\Delta_g)$ produced by acridine with each laser pulse: (a) δ[rubrene] determined from the absorbance change at 530 nm, and (b) the lifetime of $O_2(a^1\Delta_g)$ determined both in the absence and presence of rubrene from otherwise identical samples.

In liquid samples, where the encounter frequency between the comparatively mobile sensitizer and $O_2(X^3\Sigma_g^-)$ is high, the rate of $O_2(a^1\Delta_g)$ formation is rapid. Under these conditions, the $O_2(a^1\Delta_g)$ lifetime can be determined

Table 1. ϕ_Δ Values Obtained by the Method of Chemical Trapping

solvent	conditions	ϕ_Δ (acridine)
toluene	air saturated	0.73 ± 0.13
polystyrene	air saturated	0.58 ± 0.09
polystyrene	oxygen saturated	0.50 ± 0.10

directly from a fit to the decay of the time-resolved $O_2(a^1\Delta_g)$ phosphorescence signal. In solid polystyrene, however, where solute diffusion coefficients are much smaller, the rate of $O_2(a^1\Delta_g)$ formation in a photosensitized process is slow compared to the rate of $O_2(a^1\Delta_g)$ disappearance.[1,14] Under these conditions, it is necessary to deconvolute the decay kinetics of the $O_2(a^1\Delta_g)$ precursor from the observed time-resolved $O_2(a^1\Delta_g)$ phosphorescence signal in order to obtain the $O_2(a^1\Delta_g)$ lifetime.[1,14] The precursor kinetics are readily obtained by monitoring the triplet-state sensitizer in a flash absorption experiment. Although the rate of triplet sensitizer decay, and consequently the rate of $O_2(a^1\Delta_g)$ formation, depends on the equilibrium ground-state oxygen concentration, the rate of $O_2(a^1\Delta_g)$ decay does not.[14] Thus, independent measurements of the $O_2(a^1\Delta_g)$ lifetime in solid polymers can be obtained from air- and oxygen-saturated samples.

From a sample containing only acridine, we recorded the information necessary to give the quantity ($k_d + k_r$). From a separate sample containing both acridine and rubrene, we simultaneously recorded, using one laser pulse (a) δ[rubrene], (b) the corresponding time-resolved $O_2(a^1\Delta_g)$ phosphorescence signal, and (c) the laser energy. With a second laser pulse and using the same sample, the rate of ^{3}acridine decay was recorded in a flash absorption experiment (λ_{obs} = 440 nm). The latter was used to obtain the quantity ($k_d + k_r + k_{rxn}$[rubrene]) by deconvolution. These data were sufficient to make a ϕ_Δ determination.

Values of ϕ_Δ thus obtained were dependent on the incident photolysis energy E_L.[40] This phenomenon is not uncommon when pulsed lasers are used as the photolysis source, where nonlinear effects can contribute at high incident energies.[3,41] Quantum yield data reported in Table 1 are for an average incident laser energy of 1.3 mJ/pulse. Errors reported are the standard deviation to the mean value of independent measurements. Our determination of ϕ_Δ(acridine) in toluene is consistent with values reported in the literature in which benzene was used as the solvent [($\phi_\Delta^{benzene}$ (acridine) = 0.83 ± 0.06].[3]

Method 2. Relative Intensity of $O_2(a^1\Delta_g)$ Phosphorescence. Description of the method. In this method, the intensity of the acridine-sensitized $O_2(a^1\Delta_g)$ phosphorescence recorded from a sample of solid polystyrene was compared to that recorded from a solution of toluene, for which ϕ_Δ is known. The data were recorded from otherwise identical samples under identical conditions (i.e., samples of the same dimension and identical absorbance at the photolysis wavelength). The integrated time-resolved $O_2(a^1\Delta_g)$ phosphorescence signal intensity (I_Δ) is proportional to the total number of photons emitted by $O_2(a^1\Delta_g)$ which, in turn, is proportional to ϕ_Δ (eq 9).

$$I_\Delta = \kappa n^{-2} \phi_\Delta k_r \tau_\Delta E_L (1 - 10^{-A}) \qquad (9)$$

The product of the photolysis laser pulse energy (E_L) and the factor ($1 - 10^{-A}$) is proportional to the number of photons absorbed by acridine in a system whose absorbance at the excitation wavelength is A. As in eq 2, the product of the rate constant for $O_2(a^1\Delta_g)$ radiative decay (k_r) and the $O_2(a^1\Delta_g)$ lifetime (τ_Δ) represents the fraction of $O_2(a^1\Delta_g)$ that, once formed, decays by emitting a photon. Embodied in the instrument constant κ are parameters that, for example, reflect the efficiency of light collection and the gain of the detection system. n is the refractive index of the medium from which the $O_2(a^1\Delta_g)$ phosphorescence originates. In our treatment, the factor n^2 is included in eqs 9 and 10 in order that we may compare data recorded from liquid toluene with those recorded from solid polystyrene. This correction factor is necessary for a measurement in which the optical detector is in air (n = 1) and the luminescence originates in a different medium ($n > 1$).[26]

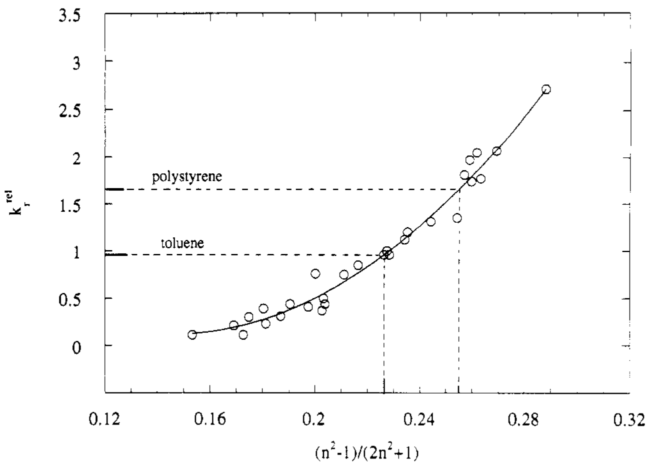


Figure 3. A plot of the relative rate constant for $O_2(a^1\Delta_g)$ radiative deactivation (k_r^{rel}) vs the electronic polarizability of the solvent in which k_r^{rel} was determined. The polarizability is expressed in terms of the refractive index n of the medium. Indicated on the plot are (a) the toluene data, and (b) the k_r^{rel} value expected for polystyrene.

The desired quantity ϕ_Δ for a given medium m can thus be obtained by rearranging eq 9. The quantities k_r^m and

$$\phi_\Delta^m = \frac{(n^m)^2 I_\Delta^m}{\kappa k_r^m \tau_\Delta^m E_L (1 - 10^{-A})} \qquad (10)$$

κ are difficult to measure directly. However, κ is independent of solvent and will therefore cancel when the ratio $\phi_\Delta^{PS}/\phi_\Delta^{TOL}$ is determined from data recorded under otherwise identical conditions. Unlike κ, however, k_r^m is solvent dependent.[26] Thus, an attempt to determine $\phi_\Delta^{PS}/\phi_\Delta^{TOL}$ requires that we know k_r^{TOL}/k_r^{PS}. Values of k_r determined in liquid solvents correlate with the solvent electronic polarizability, which, in turn, can be expressed in terms of the solvent refractive index n, obtained at an optical frequency.[26] These data are shown in Figure 3.[42,43] We have independently shown that a solid-phase matrix such as polystyrene influences the overall rate of $O_2(a^1\Delta_g)$ deactivation ($k_d + k_r$) in much the same way as a liquid-phase solvent system.[1,14] Thus, if the value of k_r in polystyrene were to follow the same trend illustrated in Figure 3, the ratio k_r^{TOL}/k_r^{PS} should equal 0.57 ± 0.05. In determining this ratio of radiative rate constants, the values of n used for toluene and polystyrene, n^{TOL} = 1.497 and n^{PS} = 1.6, were measured directly for our samples and are consistent with published values of the refractive index.

The Measurements. The integrated $O_2(a^1\Delta_g)$ phosphorescence intensity I_Δ was measured as a function of the energy absorbed from the photolysis laser pulse [$E_L(1 - 10^{-A})$] in solid polystyrene and liquid toluene samples that contained acridine as the sensitizer. In these measurements, average values for the $O_2(a^1\Delta_g)$ lifetime were τ_Δ^{TOL} = 29.4 ± 0.9 μs and τ_Δ^{PS} = 22 ± 1 μs, which are in excellent agreement with published values in the

Table 2. ϕ_Δ Values Obtained by the Method of Comparing $O_2(a^1\Delta g)$ Phosphorescence Intensities

sensitizer	k_q (M^{-1} s^{-1})[a]	τ_T^{PS} (N_2)[b]	τ_T^{PS} (air)[b]	$\phi_\Delta^{PS}/\phi_\Delta^{TOL}$
Acridine	$<4 \times 10^3$	25 ms	33 µs	0.71 ± 0.07
RB[c]	1.3×10^7	180 µs	28 µs	0.62 ± 0.06
MP9[d]	2.8×10^6		28 µs	0.59 ± 0.06

[a] The rate constant for the quenching of $O_2(a^1\Delta_g)$ by the sensitizer itself. Measured in liquid CS_2 (acridine and MP9) and CH_3CN (RB). [b] The sensitizer triplet-state lifetime in solid polystyrene. Under nitrogen, the triplet state decay was single exponential. Under air, however, the decay was best described with a biexponential fitting function. This is consistent with previously published data.[14] The value of τ_T(air) listed is the longest of the corresponding two lifetimes. [c] The ^{1}RB lifetime is short enough that oxygen-induced intersystem crossing does not play a large role in the liquid, where diffusion coefficients are large. Thus, ^{3}RB yields are expected to be approximately the same in both the liquid and solid solvents. [d] MP9 has a comparatively high triplet quantum yield ($\phi_T = 0.8$) in the absence of oxygen. Thus, despite a singlet-state lifetime ($\tau_s \approx 19$ ns) that results in a slightly larger component of oxygen-induced intersystem crossing in the liquid, yields of ^{3}MP9 are approximately the same in both the liquid and solid.[28,44]

respective media.[1,14] Incorporating data on k_r and n, the ratio $\phi_\Delta^{PS}/\phi_\Delta^{TOL}$ was then calculated by using eq 10. As observed in method 1, ϕ_Δ values likewise varied with the laser power. This was manifested as a slight nonlinear dependence of I_Δ with respect to $E_L(1 - 10^{-A})$. For consistency with the chemical trapping data, $\phi_\Delta^{PS}/\phi_\Delta^{TOL}$ ratios were calculated for data at an incident laser energy of 1.3 mJ/pulse (Table 2).

If we assume that $\phi_\Delta^{benzene}$ (acridine) = 0.83 ± 0.06 (as recently published in a compilation of $O_2(a^1\Delta_g)$ quantum yields)[3] is also valid in toluene, then multiplication of this quantity by the $\phi_\Delta^{PS}/\phi_\Delta^{TOL}$ ratio in Table 2 yields ϕ_Δ^{PS} (acridine) = 0.59 ± 0.10, which is in accord with the data reported in Table 1.

In similar experiments, in which the relative intensities of $O_2(a^1\Delta_g)$ phosphorescence were compared, we measured the ratio $\phi_\Delta^{PS}/\phi_\Delta^{TOL}$ for the sensitizers MP9 and a rose bengal derivative (RB). These data are also listed in Table 2.

Discussion

Quantum yield measurements are characteristically susceptible to experimental error. Thus, if possible, it is prudent to measure the same quantity by using several independent techniques. In this study, we determined ϕ_Δ^{PS}(acridine) by (1) using a chemical trapping reaction to quantify the amount of $O_2(a^1\Delta_g)$ produced per photolysis photon, and (2) comparing the intensity of acridine-sensitized $O_2(a^1\Delta_g)$ phosphorescence observed from a polystyrene sample to that observed from toluene for which ϕ_Δ(acridine) is known. Results from the first method are consistent with those obtained from the second method and, upon averaging, yield ϕ_Δ^{PS}(acridine) = 0.56 ± 0.05. [The reported error is the standard deviation from the mean.]

For each method employed to quantify ϕ_Δ^{PS} (acridine), an assumption was required in the analysis that could potentially limit the accuracy of the data thus obtained. In the chemical trapping experiment (method 1), it was assumed that, in the polymer, rubrene removes $O_2(a^1\Delta_g)$ only by reaction [i.e., the rubrene-induced physical deactivation of $O_2(a^1\Delta_g)$ to $O_2(X^3\Sigma_g^-)$ is not significant]. We independently showed that, in toluene, rubrene indeed removes $O_2(a^1\Delta_g)$ by reaction only. However, if the behavior of rubrene in the polymer differs from that in the liquid, such that $O_2(a^1\Delta_g)$ can be quenched without reaction to form the endoperoxide, then the true value of ϕ_Δ^{PS}(acridine) will be greater than that reported in Table 1. In the experiments where the relative intensity of $O_2(a^1\Delta_g)$ phosphorescence was monitored (method 2), we assumed that the rate constant k_r for the radiative transition $O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-)$ in solid polystyrene could be estimated from corresponding liquid-phase data. Because ϕ_Δ^{PS}(acridine) values obtained by using these two independent approaches are similar, we conclude that both of these assumptions are indeed valid. Specifically, (1) in solid polystyrene, rubrene removes $O_2(a^1\Delta_g)$ by chemical reaction only, and (2) the solid polymer influences the $O_2(a^1\Delta_g)$ radiative lifetime in much the same way as does a liquid solvent.

The data in Tables 1 and 2 indicate that under our experimental conditions ϕ_Δ^{PS}(acridine) is slightly smaller than ϕ_Δ^{TOL}(acridine). The following points help in the interpretation of this result:

(1) Because solute diffusion coefficients are smaller in the solid polymer, it is important to ascertain whether or not the polymer data reflect a less efficient scavenging of the acridine triplet state by oxygen. Changes in the triplet-state lifetime upon the admission of oxygen, however, indicate that in both the solid and liquid, 99.9% of the acridine triplets are quenched by $O_2(X^3\Sigma_g^-)$.[45] [The lifetime of ^{1}acridine in both media is short enough to preclude quenching by oxygen.[27,28]]

(2) We have shown that, for reactions not limited by diffusion, the quenching of $O_2(a^1\Delta_g)$ by an added solute, or by the sensitizer itself, can be more effective in glassy polymers than in liquid solvents.[16,31,35] This phenomenon likely derives from the more rigid solvent cage of the glass, which allows for more collisions between the oxygen–quencher pair prior to dissociation. From this perspective, it is reasonable to postulate that the inequality ϕ_Δ^{PS} (acridine) < ϕ_Δ^{TOL} (acridine) may be due to enhanced in-cage $O_2(a^1\Delta_g)$ quenching by the sensitizer in the solid. If so, one might expect $\phi_\Delta^{PS}/\phi_\Delta^{TOL}$ to be smaller for sensitizers that can more efficiently quench $O_2(a^1\Delta_g)$. However, data recorded for the sensitizers mesoporphyrin IX dimethyl ester (MP9) and a rose bengal derivative (RB), both of which have rate constants for $O_2(a^1\Delta_g)$ quenching that are ~3 orders of magnitude larger than that of acridine, indicate that this effect, at most, plays only a modest role (Table 2).

The inequality ϕ_Δ^{PS}(acridine) < ϕ_Δ^{TOL}(acridine) may derive from (a) a quantum yield of triplet state sensitizer ϕ_T or (b) a fraction f_Δ^T, either of which is slightly smaller in the solid than in the liquid. We are not aware of data that specifically address the ϕ_T issue. Although the MP9 and RB experiments described above partly address the f_Δ^T issue, other phenomena can influence k_{et}^3 and k_q^3. For example, in liquids, f_Δ^T depends on the extent to which charge-transfer (CT) character is mixed into the ^{3}sens–$O_2(X^2\Sigma_g^-)$ complex:[44,46] more CT character lowers $O_2(a^1\Delta_g)$ yields. Data from a study of magnetic field effects on the oxygen–organic molecule (M) photosystem indicate that, in solid polymers, where M and O_2 are held in close proximity for a longer time, low-lying states of the M–O_2 complex are better able to acquire CT character.[47] Thus, the inequality ϕ_Δ^{PS}(acridine) < ϕ_Δ^{TOL}(acridine) may reflect the medium-dependent extent to which the ^{3}sens–O_2 complex is influenced by the CT state.

Our results differ only slightly from those of Krasnovskii et al.,[20] but are substantially different from those of Byteva et al.[22] (*vide supra*). Specifically, for a variety of sensitizer/polyester systems, the data of Byteva et al. indicate that the yield of $O_2(a^1\Delta_g)$ is over 3 orders of magnitude smaller in the polymer than in CCl_4. Because details about the Krasnovskii/Byteva systems are lacking, we can only speculate as to the origin of these differences. For example, in the systems studied by Byteva, the rather large liquid/solid solvent effect could partly reflect a change in bimolecular rate constants (eqs 1a and 1b).[45] By choosing acridine as a $O_2(a^1\Delta_g)$ sensitizer, we created a system that was not sensitive to diffusion-dependent changes in the bimolecular quenching rate constants. The Byteva/Krasnovskii data could also partly reflect more subtle effects that derive from a liquid solvent that is not exactly a molecular analog of the polymer. For example, the extent to which the data are influenced by the sensitizer/oxygen charge-transfer state may be more pronounced for a solvent pair other than polystyrene/toluene. There are also experimental phenomena that could indicate an apparent $O_2(a^1\Delta_g)$ yield which is smaller than the "true" ϕ_Δ value. For example, when monitoring $O_2(a^1\Delta_g)$ phosphorescence from thin polymer films, poor signal-to-noise ratios can preclude an accurate ϕ_Δ measurement. Indeed, Byteva et al. acknowledge that this is a problem in their study. Secondly, it is essential that the photosensitizing dye be homogeneously distributed throughout the polymer sample, as is the case in the liquid to which the polymer data are compared. Byteva et al. likewise acknowledge that the method they used to incorporate dye molecules into the polymer film yielded samples whose "coloration was very uneven". Finally, phenomena that result in an $O_2(X^3\Sigma_g^-)$ concentration that is smaller in the polymer than in the liquid could also give rise to an apparent $O_2(a^1\Delta_g)$ yield that is too small. Such phenomena include (a) different $O_2(X^3\Sigma_g^-)$ solubilities in the polymer and liquid, (b) a polymer that does not rapidly reach equilibrium with the ambient atmosphere due to a small oxygen diffusion coefficient, and (c) depletion of oxygen in the polymer matrix during the course of the measurement by a reaction with, for example, the matrix.

One objective of our ϕ_Δ study was to provide more insight into the potential contribution of $O_2(a^1\Delta_g)$ in photooxygenation reactions in a solid matrix. Specifically, if the $O_2(a^1\Delta_g)$ yield were inherently much less in a glassy polymer than in a liquid, then $O_2(a^1\Delta_g)$ would not likely be an important intermediate in photoinduced reactions that degrade either the macromolecule or low molecular weight additives within such solid matrices. Whatever the reasons for the slightly lower ϕ_Δ value obtained in the polystyrene matrix under our conditions, it is clear that a photosensitized process in a solid, air-saturated polymer can indeed produce a substantial amount of $O_2(a^1\Delta_g)$.

Acknowledgment. This work was supported by the Department of Energy under contract DE-AC04-4AL85000 and by a grant from the Army Research Office.

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$O_2(a^1\Delta_g)$ in solid polystyrene will be even closer to that in toluene, and the difference between these values is not likely to be significant.

(41) At higher incident laser powers, despite efficient quenching of ^{3}acridine by $O_2(X^3\Sigma_g^-)$, it is possible that lower $O_2(a^1\Delta_g)$ yields may result from (a) an "inner-filter" effect in which absorption by ^{3}acridine effectively shields ground-state acridine from the incident light, and (b) depletion of the initial ^{3}acridine population by multiphoton absorption to form species that are not $O_2(a^1\Delta_g)$ precursors.

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