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Time-Resolved Luminescence Measurements of Triplet-Sensitized Singlet-Oxygen Production: Variation in Energy-Transfer Efficiencies

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Abstract: Acridine, 2-acetonaphthone, and benzophenone have been subjected to pulsed-laser excitation at 355 nm in aerated benzene. In each case, the sensitizer-triplet yield and singlet-oxygen, $O_2(^1\Delta_g)$, infrared-luminescence intensity have been monitored by kinetic absorption and kinetic emission spectroscopy, respectively. The data have confirmed that the quenching of high-energy triplets by ground-state oxygen, $O_2(^3\Sigma_g^-)$, does not yield $O_2(^1\Delta_g)$ with unit efficiency in all cases. For example, 2-acetonaphthone and benzophenone are respectively only 70% and 30% as efficient in this respect as is acridine.

I. Introduction

The nature of the processes whereby electronically excited singlet and triplet states interact with ground-state oxygen, $O_2(^3\Sigma_g^-)$, has been the subject of considerable discussion over the last 15 years.[1-21] Singlet quenching may proceed via reactions 1 and 2, operation of the former being dependent upon an S_1–T_1 energy gap larger than that of the $O_2(^1\Delta_g)$ excitation energy of 7882 cm^{-1}. Both may thus contribute to the process termed oxygen-induced intersystem crossing, which is thought to proceed with unit efficiency in hydrocarbon solvents.[9]

$$^1S^* + O_2(^3\Sigma_g^-) \rightarrow {}^3S^* + O_2(^1\Delta_g) \tag{1}$$

$$^1S^* + O_2(^3\Sigma_g^-) \rightarrow {}^3S^* + O_2(^3\Sigma_g^-) \tag{2}$$

$$^3S^* + O_2(^3\Sigma_g^-) \rightleftarrows {}^1[S\cdots O_2]^* \rightarrow S + O_2(^1\Delta_g) \tag{3}$$

$$^3S^* + O_2(^3\Sigma_g^-) \rightleftarrows {}^3[S\cdots O_2]^* \rightarrow S + O_2(^3\Sigma_g^-) \tag{4}$$

$$^3S^* + O_2(^3\Sigma_g^-) \rightleftarrows {}^5[S\cdots O_2]^* \tag{5}$$

In this paper we present no data to dispute this contention regarding singlet states. The nature of the oxygen quenching of triplet states is, in contrast, a current source of controversy. The two spin-allowed processes are represented by reactions 3 and 4 which proceed via the singlet and triplet states of the encounter complex, respectively. Quenching via the quintet state (eq 5) is forbidden on both spin and energy grounds.[12] Rate constants for oxygen quenching of aromatic hydrocarbon triplets (1–30×10^9 L mol^{-1} s^{-1})[12] do not generally exceed one-ninth of the diffusion-controlled value, and it was thus concluded[12] that quenching proceeds exclusively via the singlet encounter complex (eq 3) and that each quenching act leads to a molecule of $O_2(^1\Delta_g)$.[22] These data supported conclusions reached on the basis of a steady-state photooxidation study.[6] In direct constrast to the above conclusions, we[17] and Garner and Wilkinson[18] have shown that oxygen quenching of a variety of triplet states does not always lead to $O_2(^1\Delta_g)$ with unit efficiency. In our pulse radiolysis work based on the diphenylisobenzofuran (DPBF) bleaching technique it was found that the fraction of quenching acts leading to $O_2(^1\Delta_g)$, the S_Δ $(=k_3/(k_3 + k_4))$ value, varied from 0.4 for benzophenone to 0.9 for *p*-terphenyl. Garner and Wilkinson,[18] using energy transfer from $O_2(^1\Delta_g)$ to β-carotene as the monitoring technique, again observed low $O_2(^1\Delta_g)$ production for benzophenone (58%) relative to anthracene. The particular inefficiency of benzophenone was subsequently confirmed by steady-state experiments involving comparison with the sensitizers acridine and anthracene.[19]

Table I. Photophysical Properties of Individual Sensitizers

sensitizer	τ_s, ns	$\Phi_\Delta{}^S$	$\Phi_{ISC}{}^d$	$\lambda_{max}{}^{T\rightarrow T}$,^{d} (nm)
acridine	0.9[a]	0.03	0.73	440
2-acetonaphthone	<1.5[b]	<0.04	0.84	430
benzophenone	0.005[c]	0.00	1.0	532.5

[a] Reference 30. [b] Reference 31. [c] Reference 32. [d] Reference 33.

Recently, Stevens, Marsh, an Barltrop[20] have refuted conclusions of ourselves and Garner and Wilkinson on the basis of steady-state experiments. In particular these authors have claimed that the quenching of benzophenone triplet by oxygen yields $O_2(^1\Delta_g)$ with *unit efficiency*. In the light of such claims we have addressed ourselves to the problem of determining $O_2(^1\Delta_g)$ yields by the most direct means available, i.e., by time-resolved measurements of $O_2(^1\Delta_g)$ luminescence.[24-29] The results completely

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(22) It is to be emphasized that in this work we are concerned with quenching processes that are substantially exothermic with respect to $O_2(^1\Delta_g)$ production. In the case of the stilbenes and related molecules, for which the S_0–T_1 energy gap at the T_1 equilibrium geometry is certainly less than 7882 cm^{-1}, rate constants in benzene as high as 6–9×10^9 L mol^{-1} s^{-1} have been reported.[23] This has been attributed to the proximity of the energy surfaces, crossover to S_0 via the triplet-encounter complex (eq 4) being favored since dissipation of only a small amount of energy is required.[21]

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substantiate our previous findings that the efficiency of $O_2(^1\Delta_g)$ production can vary with sensitizer and that benzophenone is particularly inefficient in this respect.

II. Determination of Yields

We have chosen for examination the three sensitizers shown in Table I. Our aim was to excite each in aerated benzene by means of the third harmonic (355 nm) of a Q-switched Nd:YAG laser. Measurement of the $^3S^*$ triplet–triplet absorption in conjunction with published extinction coefficients would allow determination of $^3S^*$ yields in the aerated medium. In addition, measurement of the relative intensities of $O_2(^1\Delta_g)$ luminescence would provide a direct measure of the relative yields of this species formed from each sensitizer. This information is enough to provide *relative* S_Δ values for given triplet sensitizers provided the following factors are taken into consideration:

(1) The operation of reaction 1 represents a contribution to the $O_2(^1\Delta_g)$ yield that is not derived via $^3S^*$. We have thus chosen sensitizers which, apart from having significant absorption at 355 nm, have short singlet lifetimes. In Table I are shown $\Phi_\Delta{}^S$ values which are the maximum possible $O_2(^1\Delta_g)$ quantum yields for reaction via process 1, calculated using the τ_S values quoted and assuming (a) that reaction 2 does not operate and (b) that reaction 1 proceeds with a diffusion-controlled rate constant in benzene of 1.55×10^{10} L mol^{-1} s^{-1} at an oxygen concentration of 2.0×10^{-3} mol L^{-1} for the aerated solvent.[34] These $\Phi_\Delta{}^S$ values are clearly insignificant, and in any case a $O_2(^1\Delta_g)$ contribution from the singlet manifold (reaction 1) would *increase* the measured S_Δ value, thus masking energy-transfer inefficiencies within the triplet manifold.

(2) The triplet state produced as a result of intersystem crossing will be quenched by oxygen to an extent determined by competition between the rate of decay of the triplet in dearated benzene under the prevailing conditions of sensitizer concentration and light intensity and the oxygen quenching rate in the aerated medium. It is therefore necessary to ascertain whether or not, under the conditions of a particular experiment, all triplets are being scavenged by oxygen.

(3) In work of this kind it is currently not possible to place $O_2(^1\Delta_g)$ yields on an absolute basis, whether or not an accurate emission quantum yield can be determined (cf. ref 35). However, relative intensities, I_Δ, measured as voltage signals proportional to the maximum light-induced diode current may be used to give $I_\Delta/[^3S^*]_{scav}$ values which represent relative $O_2(^1\Delta_g)$ sensitization efficiencies under a given set of experimental conditions, indentical laser intensity, sensitizer optical density, light-collection geometry, etc.

III. Experimental Section

1. Laser Excitation. The reaction cells, 1-cm^2 fluorescence cuvettes, for emission and absorption experiments were placed in permanent mountings arranged one behind the other in the laser light path. The emptying and filling of the cuvettes was achieved by suction to avoid alignment changes. Excitation of target solutions in the absorption (rearmost) cuvette was carried out with the luminescence cuvette empty. This introuded only a 5% diminution of the laser light incident at the absorption position. Absorption and emission experiments were performed alternately and showed good reproducibility. Sensitizer excitation was by absorption of the third harmonic (355 nm) of the 10-ns light pulse of a Quantel YG 481 Nd:YAG laser. The unfocussed 8-mm beam was attenuated by means of a 6.4% neutral density filter such that the total energy incident at the cuvette was ca 4 mJ. Kinetic absorption spectrometry of sensitizer triplet states was performed with use of a pulsed xenon analyzing lamp at 90° to the laser beam. Monochromator slit widths were confined to give spectral bandwidths of less than 2.5 nm. Time-dependent currents produced at the anode of a Hamamatsu R928 photomultiplier were applied to the 50 Ω input connector of a Biomation 8100 digitizer coupled to PDP 11/70 computer, leading to a system risetime of ca. 2 ns. The computer-controlled data collection and analysis system has been described elsewhere.[36] The $O_2(^1\Delta_g)$ emission in the infrared was detected at 90° to the laser beam by means of 5-mm^2 Judson germanium diode mounted as previously described.[29] The diode output was applied to the 50 Ω input of the Biomation digitizer via a Judson 50dB amplifier and a Comlinear 150 MHz, 20dB impedance-matching amplifier. Application of a small reverse-bias voltage to the diode improved detection response time to ~600 ns.

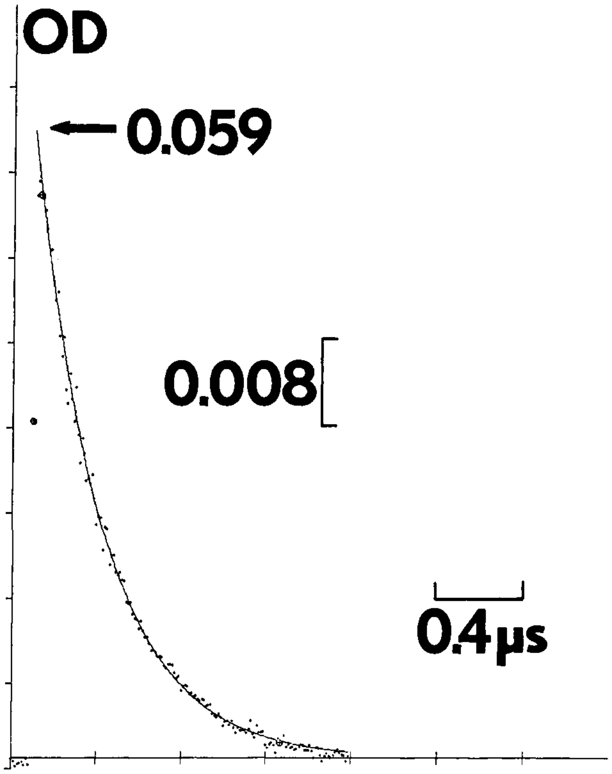

Figure 1. Exponential decay of the absorption of the 2-acetonaphthone triplet monitored at 430 nm after absorption of a 10-ns laser pulse at 355 nm by 2-acetonaphthone (OD_{355} = 1.0) in aerated benzene.

Table II. Half-Lives for Triplet Decay in Aerated and Deaerated Benzene

sensitizer	$t_{1/2}$- (aerated), μs	$t_{1/2}$- (deaerated), μs	scavenged triplet, %
acridine	0.15	32.7[a]	>99
2-acetonaphthone	0.23	18.4[a]	>98
benzophenone	0.15	3.7	96

[a] Measured as first half-life—see text.

2. Materials. Benzene (MCB Omnisolve) was used as received. Acridine ($C_6H_5CH_3$), 2-acetonaphthone (EtOH), and benzophenone (EtOH) were recrystallized.

IV. Results and Discussion

In the light of the consideration outlined in section II, we have determined the triplet yield at the end of the laser pulse, $[^3S^*]_0$, the oxygen-scavenged triplet yield, $[^3S^*]_{scav}$, and the initial luminescence intensity, I_Δ, following laser excitation of each sensitizer under carefully standardized conditions.

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Table III. Sensitizer Triplet Yields, $O_2(^1\Delta_g)$ Emission Intensities, and Relative Energy-Transfer Efficiencies, S_Δ^{rel}, in Benzene

sensitizer	$OD_0^{T\rightarrow T}$	$\sum_{max}^{T\rightarrow T\,a}$	$[^3S^*]_s0^b$	$[^3St]_{scav}^b$	I_Δ^c	$I\Delta/[^3S^*]_{scav}^d$	S_Δ^{rel}
acridine	0.101	24300	4.2	4.2	145	34.5	1.00
2-acetonaphthone	0.059	10500	5.6	5.6	135	24.1	0.70
benzophenone	0.050	7630	6.8	6.5	65	10.0	0.29

[a] Reference 33; L mol^{-1} cm^{-1}. [b] 10^{-6} mol L^{-1}. [c] mV. [d] 10^6 mV L mol^{-1}.

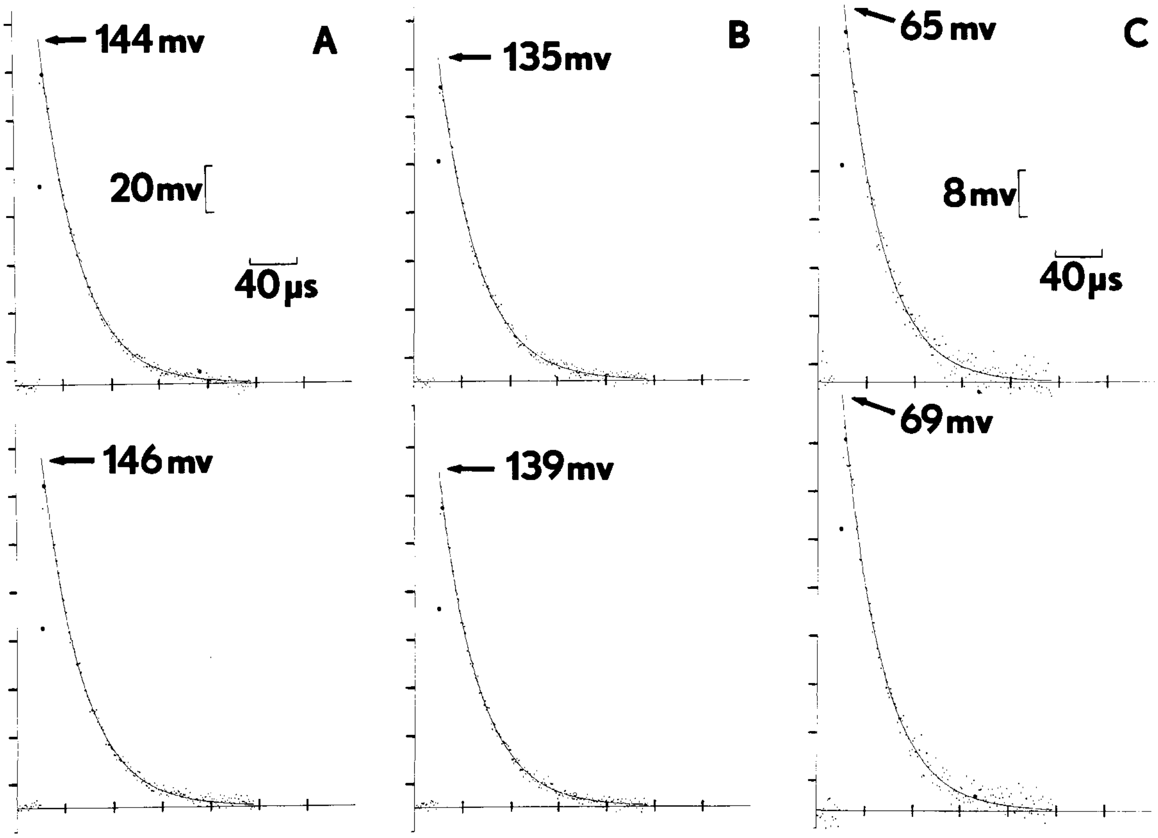

Figure 2. Exponential decay of $O_2(^1\Delta_g)$ infrared luminescence after absorption of a 10-ns laser pulse at 355 nm by sensitizers ($OD_{355} = 1.0$) in aerated (upper traces) and oxygenated benzene: (A) acridine, (B) 2-acetonaphthone, (C) benzophenone. The sensitivity and time scale are identical for parts A and B.

1. **Sensitizer Triplet Yields.** Both aerated and deaerated (nitrogen-purged) benzene solutions of each sensitizer ($OD_{355} = 1.0$) were subjected to a 10-ns pulse of 355-nm laser light. For aerated solutions fast exponential decay of the triplet state was observed (cf. Figure 1) in each case, half-lives for decay being in the 150–230-ns range (Table II). In deaerated benzene the triplet decays of acridine and 2-acetonaphthone showed a significant second-order component, first half-lives for decay being in the tens of microseconds range (Table II). The shorter-lived benzophenone triplet decayed exponentially with a half-life identical with that anticipated on the basis of published rate constants for natural decay and self-quenching[37] (ground-state concentration 10^{-2} mol L^{-1}; $\epsilon_{355} = 100$ L mol^{-1} cm^{-1}). These data demonstrate that in aerated media virtually all of the sensitizer triplets are scavenged by oxygen (Table II). Determination of I_Δ values in aerated and oxygenated benzene (vide infra) confirms these conclusions.

For the aerated experiments, triplet optical densities, $OD_0^{T\rightarrow T}$, were determined as averages of ten shots by extrapolation to time zero (Figure 1). Triplet–triplet extinction coefficients[33] then yielded $[^3S^*]_0$ values which, as a result of the data in Table II, were assumed to equal $[^3S^*]_{scav}$ values apart from the case of benzophenone where the appropriate correction was made. These values are listed in Table III.

2. **$O_2(^1\Delta_g)$ Emission Intensities.** Under experimental conditions identical with those described in the previous section we have measured the infrared luminescence of $O_2(^1\Delta_g)$ produced by quenching of sensitizer excited states in aerated benzene. For the three sensitizers employed, the lifetime of this species in benzene varied between 31 and 33 μs, in excellent agreement with published values ranging from 27 to 32 μs.[26,28,38,39] The initial I_Δ values listed in Table III were determined as averages of ten shots by extrapolation of the best fit to time zero (Figure 2). These data, taken in isolation, prove conclusively that the efficiency of $O_2(^1\Delta_g)$ production varies from sensitizer to sensitizer. To exemplify this point, the experimental emission decays in aerated benzene are shown in Figure 2 (upper traces) together with the corresponding data for *oxygen-saturated* solutions (lower traces). As mentioned, the three sensitizers have short singlet lifetimes (Table I) and contributions from reaction 1 must be negligible. The known Φ_{ISC} values (Table I) show that the ordering of the triplet yields in our experiments has to be acridine < 2-acetonaphthone < benzophenone, and yet under conditions where >96% of the triplet states are scavenged by oxygen the $O_2(^1\Delta_g)$ yields (as indicated by the infrared luminescence intensity at time zero) are reversed, markedly so for benzophenone (see Figure 2 and Table III). The

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(39) In a previous paper[19] involving two of us, A.A.G. and I.H., it was reported that $O_2(^1\Delta_g)$ is quenched by benzophenone with a rate constant of 1.8×10^7 L mol^{-1} s^{-1}, a surprising result which was at the time double checked. We have since shown that benzophenone does not significantly quench $O_2(^1\Delta_g)$, $k_q < 2 \times 10^5$ L mol^{-1} s^{-1}. We are unable to explain this error and can only withdraw the reported value[19] unreservedly. The conclusions of that piece of work are not significantly affected.

data for oxygen-saturated solutions confirm this result. The very small increases in emission intensity at time zero support the conclusions (section IV.1) concerning the minimal percentages of triplet which are not scavenged by oxygen in aerated benzene. Our $[^3S^*]_0$ values (Table III) confirm the ordering of triplet yields inferred above.

3. Relative S_Δ Values. In Table III are reproduced $I_\Delta/[^3S^*]_{scav}$ values for the three sensitizers in aerated benzene. These have been converted to relative S_Δ values by normalization to 1.0 for acridine. It can be seen that benzophenone is by far the least efficient and that 2-acetonaphthone shows intermediate efficiency. These parameters were determined in aerated as opposed to oxygenated benzene because extrapolation to time zero of the fast triplet decays in oxygen-saturated benzene would have introduced unacceptable errors (see below).

4. Consideration of Errors. While there is no doubt (section IV.2) that this work clearly demonstrates that the efficiency of $O_2(^1\Delta_g)$ may vary from sensitizer to sensitizer, questions may be raised concerning errors involved in determining the relative S_Δ values.[40] With respect to such questions we would make the following comments.

The main sources of error in the determination of $[^3S^*]_0$ come from (1) the extrapolation of the triplet absorption to time zero and (2) the use of published triplet–triplet extinction coefficients.

(1) In our experiments benzophenone triplet had the lowest measured absorbance as a consequence of its low extinction coefficient and was thus subject to the greatest error in determining $[^3S^*]_0$. For this sensitizer we have carried out two separate laser experiments (each an average of ten shots) and subjected the averaged traces to fitting procedure variations. All of the thus-derived $OD_0/^{T\rightarrow T}$ values were in the range 0.0520 ± 0.0012, a better than ±3% reproducibility. The same procedure was applied to each sensitizer.

(2) Although there are significant variations in published triplet–triplt extinction coefficients, the most systematic work in this area is that of Bensasson and Land (cf. ref 33 and references therein). Although the absolute values of their triplet–triplet extinction coefficients depend on that determined for the benzhydryl radical, we believe the relative values to be accurate and indeed have reproduced their values to ±2% using the pulse radiolysis technique for the three sensitizers under consideration.[41] Because the work described in this paper is only concerned with *relative* S_Δ values, we think that sensitizer triplet–triplet extinction coefficients are a much smaller source of error than one might at first anticipate.

It is quite clear from Table III that the yield of $O_2(^1\Delta_g)$ is the lowest for benzophenone, and the I_Δ values for this sensitizer should therefore be subject to the largest error. With use of the approach outlined above for the triplet absorbance determinations, an I_Δ value of 65.0 ± 1.6 mV was obtained for this sensitizer, a better than ±3% reproducibility.

In the light of the above considerations, we place the experimental error in the S_Δ values recorded in Table III at no greater than 10%. They were reproducible on a day-to-day basis to better than ±5% and are certainly subject to smaller errors than are previously published determinations.[17–20,42]

V. Conclusions

This paper describes the most direct technique to date for determining the efficiencies of triplet-energy transfer to oxygen and confirm that the quenching of high-energy triplets does not necessarily lead to $O_2(^1\Delta_g)$ with unit efficiency. The finding that benzophenone is particularly inefficient in this respect is in disagreement with the conclusions of Stevens, Marsh, and Barltrop, who have reported that the quenching of this sensitizer by oxygen gives $O_2(^1\Delta_g)$ with unit efficiency.[20] In order to accommodate such an interpretation of their data, these authors were forced to the conclusion that, in their work, the lifetime of triplet benzophenone in recrystallized benzene was 300 ns! Since the lifetime of this species is routinely an order of magnitude or more longer than this value, depending on solvent quality, we are convinced that their data interpretation is incorrect.

Although the S_Δ values quoted here are only relative, it seems probable that the absolute value for acridine is 1.0. Because of the short singlet lifetimes of this sensitizer, 2-acetonaphthone, and benzophenone (Table I), the S_Δ values in these three cases reflect $O_2(^1\Delta_g)$ production exclusively via the triplet state (reaction 3).

There has already been some speculation concerning the nature of the processes which result in S_Δ values of less than unity.[17,18] However, it is by no means clear whether such effects depend on varying contributions from channels 3 and 4, charge-transfer character within the encounter complex,[18] leakage of the singlet complex to ground states,[17] or a combination of these and hitherto unrecognized factors. Work on this problem is in progress.

Acknowledgment. Experiments were performed at the Center for Fast Kinetics Research (CFKR) at the Unversity of Texas at Austin. The CFKR is supported jointly by NIH Grant RR00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas at Austin. Partial support for this project came from NIH Grant GM24235 (M.A.J.R). A.A.G. and I.H. thank the Science and Engineering Research Council and the Royal Society (U.K.) for financial support.

Registry No. O_2, 7782-44-7; acridine, 260-94-6; 2-acetonaphthone, 93-08-3; benzophenone, 119-61-9.

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(40) We appreciate pertinent comments by the referees in this respect.

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(42) Since the submission of this manuscript, Das and colleagues[43] have reported an S_Δ value of 0.4 for benzophenone as a result of DPBF bleaching experiments initiated with a nitrogen laser. We have previously obtained the same value by using the same bleaching technique and initiation by pulse radiolysis.[17]

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