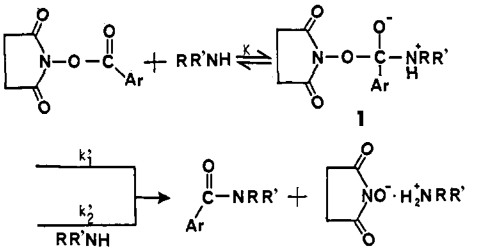
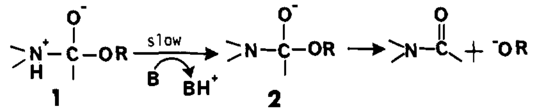
charge. Although we have no analogous data to support this argument, we favor the breakdown of the intermediate as the rate-determining step in view of the previous discussion regarding the value of β_{nuc}.

The rate expressions for both primary and secondary amines are consistent with reversible formation of a zwitterionic intermediate (**1**, eq 2) followed by rate-determining breakdown to products by either of two concurrent pathways, a general-base catalyzed, k_2', and a noncatalyzed, k_1', expulsion of NHS from the intermediate.



(2)

Work involving ^{18}O and secondary β-deuterium kinetic isotope effects[24] suggests that the transition state for noncatalyzed aminolysis involves acyl–O bond cleavage as the rate-determining step. The term representing general-base catalysis requires proton transfer in the rate-determining step. Persuasive evidence has been presented[19,24b] that proton transfer from the tetrahedral intermediate (**1**, eq 3) to the general-base catalyst, B, is rate-limiting for alkyl esters, followed by fast breakdown of the anionic intermediate **2** to products.



(3)

From the similarity in the values of β_{gb} and β values derived as a function of the pK_a of the leaving group, β_{lg}, for both alkyl and phenyl esters, it has been proposed[19] that the model of rate-limiting proton transfer is also valid for phenyl esters. Recent work,[25] however, suggests that the transition state for general-base-catalyzed decomposition of the tetrahedral intermediate of phenyl esters involves little tetrahedral character. Rather, the transition state is more nearly trigonal in nature, and thus proton transfer with the generation of a discrete intermediate cannot be rate-limiting. The greater steric requirement of phenyl vs. alkyl esters in a tetrahedral conformation has been proposed as the determinant for the change in the nature of rate-determining breakdown. If steric requirements are a decisive factor in the profile of the reaction coordinate, then NHS esters and phenyl esters may follow a similar path for this step.

The results presented in this paper, interpreted in the light of previous studies concerning the aminolysis of esters, are consistent with the view that this reaction proceeds through a tetrahedral intermediate in which the rate-determining step is the breakdown of the intermediate.

Acknowledgment. We express our sincere appreciation to Monsanto for financial support and to Dr. I. Jeng, Missouri Institute of Psychiatry, for hospitality and support extended to S.B.H. during a sabbatical when this work was conceived and to G.W.C. during the first stages of this study.

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Aromatic Ketone–Naphthalene Systems as Absolute Standards for the Triplet-Sensitized Formation of Singlet Oxygen, $O_2(^1\Delta_g)$, in Organic and Aqueous Media: A Time-Resolved Luminescence Study

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Abstract: Triplet states of simple aromatic hydrocarbons, naphthalene, biphenyl, and fluorene, have been formed with unit efficiency by triplet energy transfer from aromatic ketone triplets, themselves formed by pulsed laser excitation (355 nm) in aerated cyclohexane, dioxane, benzene, toluene, and acetonitrile. Time-resolved luminescence measurements, supported by 1,3-diphenylisobenzofuran bleaching experiments, have shown that in non-benzenoid environments the oxygen quenching of the aromatic hydrocarbon triplets gives singlet oxygen, $O_2(^1\Delta_g)$, with unit efficiency, i.e., $S_\Delta = 1.0$. In benzene and toluene this is not the case. An oxygenated benzophenone/naphthalene/micelle/water-d_2 system has been developed which produces naphthalene triplet and subsequently $O_2(^1\Delta_g)$ with unit efficiency. With appropriate controls this work has provided, for the first time, an accurate standard for the determination of $O_2(^1\Delta_g)$ quantum yields, $\phi_\Delta = \phi_T S_\Delta$, for water-soluble sensitizers which absorb at 355 nm. Naphthalene is the standard of choice in all media examined because its low triplet–triplet extinction coefficient at 355 nm maximizes the range over which the triplet yield is a linear function of the output energy of conventional Nd:YAG lasers with pulse widths in the 10–20-ns range. The establishment of naphthalene as a standard has confirmed that, under conditions producing identical $O_2(^1\Delta_g)$ yields, the emission intensity of this species is solvent dependent as a consequence of changes in the radiative rate constant, k_r.

1. Introduction

The principal mode of formation of singlet oxygen, $O_2(^1\Delta_g)$, in vivo and in vitro, involves electronic energy transfer from a sensitizer triplet-state to ground-state oxygen, $O_2(^3\Sigma_g^-)$. The quantitative aspects of such processes have been the subject of considerable discussion over the last two decades, and additional stimulus for research in this area has come from the recently developed technique of photodynamic therapy for the clinical

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treatment of cancers, a technique thought to depend on $O_2(^1\Delta_g)$ action.[1] The oxygen quenching of triplet states may proceed via the singlet or triplet states of the encounter complex (eq 1 and 2), quenching via the quintet complex being forbidden on spin

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

$$^3S^* + O_2(^3\Sigma_g^-) \rightleftarrows {}^3[S\cdots O_2]^* \rightarrow S + O_2(^3\Sigma_g^-) \qquad (2)$$

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

and energy grounds. Clearly for sensitizer $S_0 - T_1$ energy gaps of less than 7882 cm^{-1}, the electronic excitation energy requirement of $O_2(^1\Delta_g)$, quenching is restricted to the spin-exchange mechanism of eq 2, which should become more effective the closer the S_0 and T_1 surfaces. The situation for higher energy triplets (>7882 cm^{-1}) is significantly more complex. Rate constants for the oxygen quenching of aromatic hydrocarbon triplets in both benzene and hexane do not generally exceed one-ninth of the diffusion-controlled value, and it was thus concluded that quenching proceeds exclusively via channel 1 to yield $O_2(^1\Delta_g)$ with unit efficiency.[2] This agreed with theoretical predictions concerning the quenching of high-energy triplet states in general.[3] Subsequent experimentation by Garner and Wilkinson[4] and ourselves[5] using indirect time-resolved techniques to measure $O_2(^1\Delta_g)$ yields provided evidence that the oxygen quenchings of several triplet states in benzene do not lead to $O_2(^1\Delta_g)$ with unit efficiency. A lack of consensus[6] concerning the validity of our measurements involving $O_2(^1\Delta_g)$ bleaching of 1,3-diphenylisobenzofuran (DPBF) meant that confirmation had to await the advent of techniques for measuring the infrared emission of $O_2(^1\Delta_g)$ in the time-resolved mode.[7] Then, by measuring initial sensitizer triplet yields and subsequent $O_2(^1\Delta_g)$ emission yields on a relative basis it was possible to show that the efficiencies of production of $O_2(^1\Delta_g)$, the S_Δ values, for acridine, 2-acetonaphthone, and benzophenone have *relative* magnitudes of 1.0, 0.70, and 0.29.[8] Although this work conclusively showed that, for some aromatic ketone triplets at least,[9] oxygen quenching does not lead to $O_2(^1\Delta_g)$ with unit efficiency, several major obstacles still exist for both mechanistic and biological researchers in this area. Firstly, the infrared luminescence technique, although accurate, allows determination of only relative $O_2(^1\Delta_g)$ yields. Secondly, in principle, the observed $O_2(^1\Delta_g)$ emission intensity may vary with medium, not only because of changes in quantum yield, ϕ_Δ, due to solvent effects on ϕ_T and S_Δ (eq 4), but because the radiative rate constant, k_r, may

$$\phi_\Delta = \phi_T S_\Delta \qquad (4)$$

change. While changes in ϕ_T can be determined by standard techniques,[11] albeit with limited accuracy, there has been no way of differentiating between changes in S_Δ and k_r. This work addresses itself to a solution of these problems and provides absolute standards for ϕ_Δ in both hydrophobic and hydrophilic environments.

2. Experimental Section

2.1. Laser Excitation. Experiments were performed at both the Christie Hospital and Holt Radium Institute, Manchester, and the Center for Fast Kinetics Research (CFKR). Work at the Christie Hospital was carried out with a J. K. Lasers System 2000 Nd:YAG laser. The unfocused 8-mm beam was attenuated by both adjustment of the amplifier flash lamp voltage and the use of wire mesh filters. Kinetic absorption spectrometry of triplet states was essentially as previously described.[12] The $O_2(^1\Delta_g)$ emission in the infrared was detected at 90° to the laser beam by means of an E.O.S.S. Inc. G-050 5-mm^2 germanium diode. Initially the diode output, with a small reverse bias voltage to improve time response, was led via a 200-Ω load resistance to the input of a Tektronix 7A22 differential amplifier coupled to a Tektronix 7912 AD programmable digitizer. In more recent experiments the 7A22 was replaced by a Judson Model 100 preamplifier coupled to a Tektronix 7A13 differential comparator. A consequence of this difference is that earlier emission signals are recorded as μV of deflection, later ones as mV of deflection. Both systems, overall rise times ~500 ns, were based on that previously described.[7f] Digitized data were transferred to the memory of either a modified Commodore PET Series 2001-32 or a Hewlett-Packard Series 9000-216 computer for analysis. Laser excitation and kinetic absorption and emission spectroscopy carried out at the CFKR were basically as previously described.[8] The 8-mm unfocused beam was attenuated by means of a divergent lens and metal-coated filters. Computer-assisted data collection and analysis were as described;[13] emission intensity was recorded as mV of deflection. In the DPBF bleaching experiments monochromator slit widths were confined to give spectral bandwidths of less than 2.5 nm. Surfactant solutions were saturated with nitrogen or oxygen by blowing the gas onto the surface of the solution within the cuvette for several minutes.

2.2. Materials. Cyclohexane, benzene, toluene, and acetonitrile were purified as described.[5,14] Dioxane was refluxed over sodium and fractionated. Benzophenone (Bush), *p*-methoxyacetophenone, biphenyl, and naphthalene (Aldrich) were recrystallized from ethanol. Fluorene (Aldrich) was zone refined. Acetophenone and *m*-methoxyacetophenone (Aldrich) were fractionated. Uroporphyrin I dihydrochloride (Porphyrin Products Inc.), 1,3-diphenylisobenzofuran (Aldrich), water-d_2 (Aldrich, 99.8%), and sodium dodecyl sulfate (BDH, special purity) were used as received.

3. Results and Discussion

Our initial aim was to produce equal concentrations of the triplet states of a series of molecules via exothermic triplet energy transfer from a sensitizer molecule which had been selectively excited. This would avoid the introduction of errors due to inaccuracies in published ϕ_T values and/or triplet–triplet extinction coefficients. The systems chosen depended on the fact that, as a consequence of a small $S_1 - T_1$ energy gap, aromatic ketones such as benzophenones and acetophenones exhibit higher triplet energies but longer wavelength $S_0 \rightarrow S_1$ transitions than do the aromatic hydrocarbons naphthalene (N), biphenyl (B), and fluorene (F). Thus, suitable manipulation of conditions and concentrations should allow the exclusive operation of the sequence outlined in eq 5 as a consequence of ketone excitation at 355 nm. This would

$$^1\text{ketone}^* \rightarrow {}^3\text{ketone}^* \rightarrow {}^3\text{hydrocarbon}^* \rightarrow O_2(^1\Delta_g) \qquad (5)$$

then provide relative S_Δ values for the aromatic hydrocarbons. An additional advantage was that this method totally excludes interference as a consequence of oxygen-induced intersystem crossing (eq 6 and 7) since the $S_1 - T_1$ energy gap is less than 7882 cm^{-1} for benzophenones and acetophenones and ϕ_T is unity in any case.

$$^1S^* + O_2(^3\Sigma_g^-) \rightarrow {}^3S^* + O_2(^1\Delta_g) \qquad (6)$$

$$^1S^* + O_2(^3\Sigma_g^-) \rightarrow {}^3S^* + O_2(^3\Sigma_g^-) \qquad (7)$$

3.1. $O_2(^1\Delta_g)$ Formation in Organic Media. In the preliminary experiments the aromatic ketone acetophenone (AP) and its *m*-

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(8) Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1984**, *106*, 4679.

(9) Work by P. K. Das and colleagues using DPBF bleaching has clearly confirmed that, for benzophenones and acetophenones in general, S_Δ is significantly less than unity in benzene and acetonitrile.[10]

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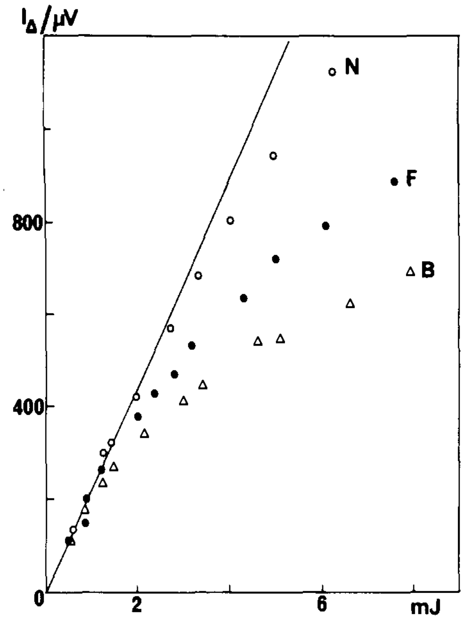

Figure 1. Emission intensity at 1270 nm extrapolated to time zero, I_Δ, against laser energy for aerated cyclohexane solutions of *p*-MAP (OD_{355} = 0.53) containing N (○), B (△), or F (●) (10^{-1} mol L^{-1}).

and *p*-methoxy derivatives (*m*-MAP and *p*-MAP) have been used as sensitizers to produce equal concentrations of N, B, and F triplets in aerated cyclohexane, benzene, and acetonitrile. In typical experiments, solutions of ketone (OD_{355} = 0.5) containing hydrocarbon (10^{-1} mol L^{-1}) were subjected to pulsed laser excitation at 355 nm with the third harmonic of a Nd:YAG laser. Given the lowest donor triplet energy, 71.8 kcal mol^{-1} for *p*-MAP[15], and the highest acceptor value, 68.0 kcal mol^{-1} for F,[15] there is no doubt that under these conditions ketone triplets are scavenged essentially exclusively by the hydrocarbons[16] whose long-lived triplets are subsequently efficiently scavenged by oxygen.[17] In all experiments $O_2(^1\Delta_g)$ emission at 1270 nm was observed (cf. Figure 3b, inset). This exhibited strictly exponential decay which was dependent on solvent but not on sensitizer. Average lifetimes, τ_Δ, for cyclohexane (24 μs), benzene (32 μs), and acetonitrile (67 μs) are to be compared with published values of 23,[18] 27–33,[7a,c,g,8,18] and 54–68 μs,[7a,c,g,18] respectively. In each case the emission intensity extrapolated to time zero, I_Δ, gave a relative measure, in microvolts or millivolts of signal (see section 2.1), of the $O_2(^1\Delta_g)$ produced as a consequence of oxygen quenching of the hydrocarbon triplets. An additional advantage of the aromatic ketone/hydrocarbon systems was that early components in the decay profiles due to sensitizer emission were avoided. All decay profiles were as shown in Figure 3b, and evaluation of I_Δ could be made cleanly and precisely.[19] This was determined as a function of laser intensity in millijoules per pulse, and significant differences were observed for the three solvents.

Cyclohexane. In Figure 1 are shown plots of I_Δ vs. laser intensity for all three hydrocarbons sensitized by *p*-MAP. Three points of immediate interest are that (a) the plots are nonlinear, (b) the degree of curvature varies in the order N < F < B, and (c) the curves are asymptotic to the same straight line which passes through the origin. We infer from these data that S_Δ has the same value for all three hydrocarbons and that this value is very probably 1.0. The curvature in the plots is a consequence of a lowering of the otherwise anticipated hydrocarbon triplet yield due to absorption of laser light by these triplet states during the pulse (vide infra).

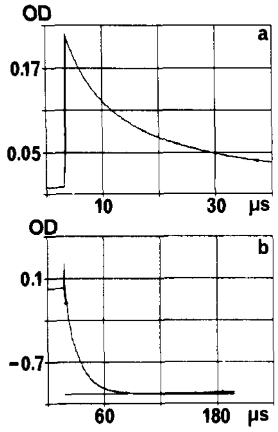

Figure 2. (a) Time dependence of $^3N^*$ absorption at 415 nm after absorption of a 6.4-mJ laser pulse at 355 nm by a deaerated solution of *p*-MAP (OD_{355} = 3.0) in cyclohexane containing N (10^{-1} mol L^{-1}). (b) Time dependence of DPBF bleaching at 410 nm after absorption of an identical laser pulse by an aerated solution of *p*-MAP (OD_{355} = 3.0) in cyclohexane containing N (10^{-1} mol L^{-1}) and DPBF (4.8×10^{-5} mol L^{-1}).

In order to support our conclusions that S_Δ = 1.0 for all three hydrocarbons in cyclohexane, we have performed DPBF bleaching experiments.[5,20] Thus, deaerated solutions of *p*-MAP (OD_{355} = 3.0) in cyclohexane containing N (10^{-1} mol L^{-1}) were subjected to pulsed laser excitation at 355 nm, and the initial $^3N^*$ yield was determined by extrapolation of its optical density to time zero (Figure 2a) and by the use of the extinction coefficient published for this solvent.[21] The decay of $^3N^*$ was largely second order under these conditions as a consequence of T–T annihilation but became cleanly first order on aeration. The respective first half-lives in the absence (12 μs) and presence (102 ns) of air confirmed that all $^3N^*$ is scavenged by oxygen in the aerated medium. In separate experiments aerated solutions, identical but for the addition of DPBF (4.8×10^{-5} mol L^{-1}), were subjected to pulsed laser excitation under the same conditions. Concentrations were such that only the processes summarized in eq 8–10

$$^3p\text{-MAP}^* \rightarrow {}^3N^* \rightarrow O_2(^1\Delta_g) \quad (8)$$

$$O_2(^1\Delta_g) \xrightarrow{k_d} O_2(^3\Sigma_g^-) \quad (9)$$

$$O_2(^1\Delta_g) + \text{DPBF} \xrightarrow{k_q} \text{loss of DPBF} \quad (10)$$

were significant. The observed bleaching of DPBF, as exemplified in Figure 2b, was restricted to less than 10%, conditions under which the first-order constant for bleaching, k', is given by eq 11. Measurement of k' and use of the average value for k_d from the luminescence experiments gave the percentage of $O_2(^1\Delta_g)$ molecules scavenged by DPBF and hence the initial $O_2(^1\Delta_g)$ concentration. Experiments of this type were performed at three laser

$$k' = k_d + k_q[\text{DPBF}] \quad (11)$$

energies covering the range shown in Figure 1. Values of S_Δ at 1.0, 3.2, and 6.4 mJ/pulse were 1.01, 1.16, and 1.00, in excellent agreement with the conclusion from Figure 1 that S_Δ = 1.0 for all three hydrocarbons. Although we would be reluctant to place error bars of less than ±15% on S_Δ values determined by the DPBF bleaching method, it is to be emphasized that they are used here

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(15) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(16) For instance, the rate constants determined by pulse radiolysis for the quenching of ^3p-MAP* by F (4.0×10^9 L mol^{-1} s^{-1}) and by oxygen (5.0×10^9 L mol^{-1} s^{-1}) in benzene show that under these conditions >97% of ^3p-MAP* is scavenged by F.

(17) Measurement of aromatic hydrocarbon triplet first half-lives in aerated and nitrogen-purged media showed that >99% of triplets were scavenged by oxygen despite a T–T annihilation contribution in the oxygen-free system.

(18) Rodgers, M. A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6201.

(19) Errors in this extrapolation procedure have been discussed[8] and are placed at no more than ±5%. In all cases of aromatic ketone/hydrocarbon sensitization of $O_2(^1\Delta_g)$ in this work, nitrogen bubbling resulted in essentially complete loss of the emission signal at 1270 nm.

(20) Adams, D. R.; Wilkinson, F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 586. Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244. Young, R. H.; Brewer, D.; Keller, R. A. *Ibid.* **1973**, *95*, 375.

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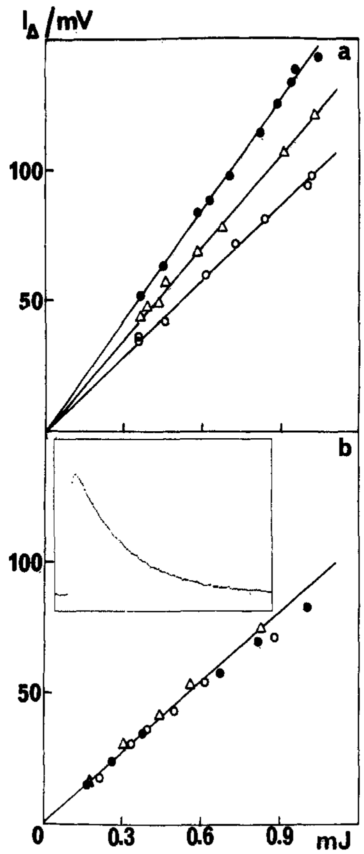

Figure 3. Emission intensity at 1270 nm extrapolated to time zero, I_Δ, against laser energy (a) for aerated benzene solutions of *p*-MAP (OD_{355} = 0.5) containing N (△), B (○), or F (●) (10^{-1} mol L^{-1}) and (b) the corresponding experiments in cyclohexane. Inset: Corresponding time dependence of emission at 1270 nm after absorption of a 0.81-mJ laser pulse by a cyclohexane solution containing F (10^{-1} mol L^{-1}); 10 mV/division, 10 μs/division; τ_Δ = 23.5 μs.

as *support* for the conclusions based on I_Δ determinations that S_Δ = 1.0 for each hydrocarbon in cyclohexane (see also next section).

Benzene. Plots of I_Δ vs. laser energy for this solvent showed less curvature than for cyclohexane (cf. section on origins of curvature and Figure 6) and clearly indicated that, in contrast to cyclohexane, S_Δ is not unity for each hydrocarbon. The validity of this conclusion is emphasized by the plots in Figure 3 which compare data obtained for (a) benzene and (b) cyclohexane at low laser energies, 0.16–1.04 mJ/pulse. All plots were essentially independent of sensitizer, and there is no doubt that in benzene the three hydrocarbons exhibit quite different S_Δ values. Virtually identical behavior was found with toluene as solvent. DPBF bleaching experiments of the type described for cyclohexane yielded identical S_Δ values for N in benzene of 0.55 ± 0.08 at laser energies of 1.0 and 3.2 mJ/pulse.

Using the above value of 0.55, we have measured an absolute value of S_Δ for benzophenone (BP) in benzene. In Figure 4 are shown plots of I_Δ vs. laser intensity for 355-nm excitation of BP (OD_{355} = 1.2) in benzene with and without N (10^{-1} mol L^{-1}). The ratio of the slopes (1.87) is the ratio of the S_Δ value for N to that for BP. Thus $S_\Delta(BP) = S_\Delta(N)/1.87 = 0.29$. This value is exactly that reported earlier[8] as a *relative* value for BP when acridine was arbitrarily taken as having S_Δ = 1.0 in benzene. This allows us to conclude that the absolute value of S_Δ for acridine in benzene is in fact unity. This result is in accord with our observations that this sensitizer produces singlet oxygen in benzene with higher efficiency than any other sensitizer so far examined. From the slopes of Figure 3a and taking $S_\Delta(N)$ = 0.55, we have evaluated S_Δ for F and B as 0.66 and 0.45, respectively.

Acetonitrile. In Figure 5 are shown the standard plots for *p*-MAP as sensitizer of N, B, and F triplets. These plots show extremely pronounced curvature, more so than in cyclohexane (Figure 1), but nevertheless it is quite clear that the three plots are asymptotic with respect to the same straight line passing through the origin. We assume therefore that, in this solvent also, S_Δ has the value of unity for each hydrocarbon.

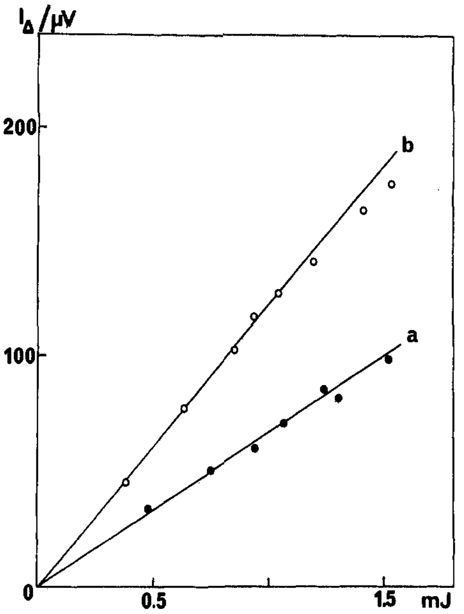

Figure 4. Emission intensity at 1270 nm extrapolated to time zero, I_Δ, against laser energy for aerated benzene solutions of (a) BP (OD_{355} = 1.2) and (b) BP (OD_{355} = 1.2) and N (10^{-1} mol L^{-1}).

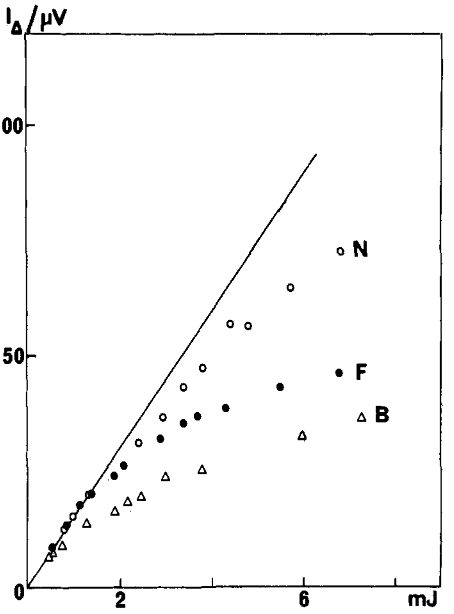

Figure 5. Emission intensity extrapolated to time zero, I_Δ, against laser energy for aerated acetonitrile solutions of *p*-MAP (OD_{355} = 0.53) containing N (○), B (△), or F (●) (10^{-1} mol L^{-1}).

Origins of Curvature in I_Δ vs. Laser Energy Plots. A consideration of the available data indicated that curvature was most apparent in the orders acetonitrile > cyclohexane ≫ benzene and B > F > N. Since it is well documented that T → T extinction coefficients are significantly smaller in benzene than in other solvents (cf. ref 11), the clear inference is that absorption of the laser light by triplet states during the 12-ns laser pulse is becoming more important as the laser energy is increased, thus lowering the anticipated triplet yield. The available literature data[21,22] which show that $^3N^*$ (λ_{max} ~ 415 nm) absorbs much less intensely at 355 nm than do $^3B^*$ (λ_{max} ~ 360 nm) and $^3F^*$ (λ_{max} ~ 380 nm)

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(22) Heinzelmann, W.; Labhart, H. *Chem. Phys. Lett.* **1969**, *4*, 20.

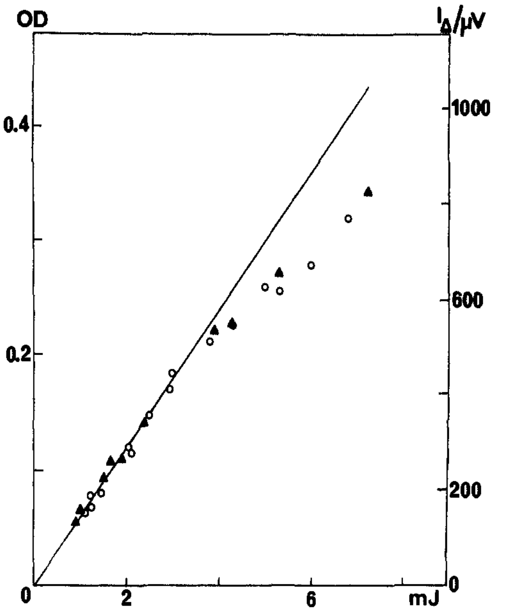

Figure 6. Naphthalene triplet optical density at 423 nm (○) and $O_2(^1\Delta_g)$ emission intensity at 1270 nm (▲), both extrapolated to time zero, as a function of laser energy. Experiments involved absorption of the 12-ns laser pulse at 355 nm by deaerated (absorption) and aerated (emission) benzene solutions of *m*-MAP (OD_{355} = 0.5) and N (10^{-1} mol L^{-1}).

are in agreement. In Figure 6 is shown a plot of the $^3N^*$ optical density, extrapolated to time zero, for laser excitation of *m*-MAP (OD_{355} = 0.5) in the presence of N (10^{-1} mol L^{-1}) in deaerated benzene, together with the corresponding I_Δ values for $O_2(^1\Delta_g)$ emission from an identical but aerated solution. These data clearly confirm the above contention that curvature in I_Δ vs. laser energy plots is a consequence of changes in triplet yields and not subsequent competing triplet reactions (T–T annihilation, for example). The insensitivity to laser energy of S_Δ values determined from DPBF bleaching experiments provides further support for these conclusions. It is to be emphasized that the origins of the curvature described have been discussed for the sakes of completeness and clarity. Such effects in no way influence the accuracy of this work since $O_2(^1\Delta_g)$ yields have been taken from strictly linear regions of I_Δ vs. laser energy plots.

3.2. $O_2(^1\Delta_g)$ Formation in Sodium Dodecyl Sulfate Micelles. The biological significance of $O_2(^1\Delta_g)$ and the importance in this respect of hydrophilic environments made extrapolation of the above work to aqueous systems highly desirable; this has been possible as a consequence of an examination of sodium dodecyl sulfate (SDS) based micellar systems. Of the ketones employed for organic media, the acetophenones do not exhibit significant absorption at 355 nm when solubilized in SDS/water. We have, therefore, been forced to sacrifice some degree of available triplet energy for the sake of significant absorption, and work in this area has of necessity been restricted to the use of BP as sensitizer. Since BP (68.6 kcal mol^{-1})[15] and F (68.0 kcal mol^{-1})[15] have very similar triplet energies, a further restriction was that only N (60.9 kcal mol^{-1})[15] and B (65.7 kcal mol^{-1})[15] could be used as aromatic hydrocarbon acceptors.

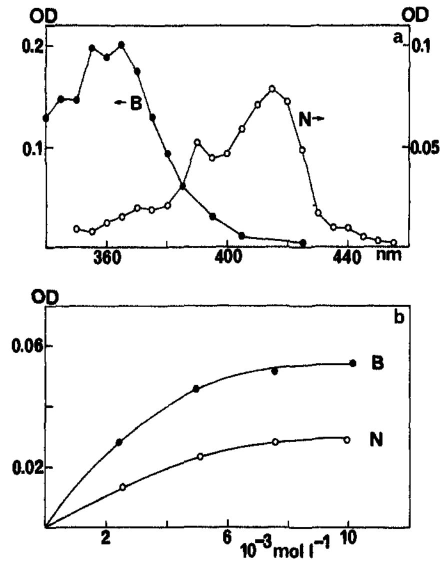

Figure 7. (a) Transient spectra 210 ns (N) and 300 ns (B) after laser excitation (16 mJ/pulse) of BP (5.9 × 10^{-3} mol L^{-1}) solubilized with aromatic hydrocarbon (10^{-2} mol L^{-1}) in aerated water solutions of SDS (0.5 mol L^{-1}). (b) Triplet optical densities extrapolated to time zero against ground-state concentration for N (415 nm) and B (380 nm) after laser excitation of BP in otherwise similar experiments.

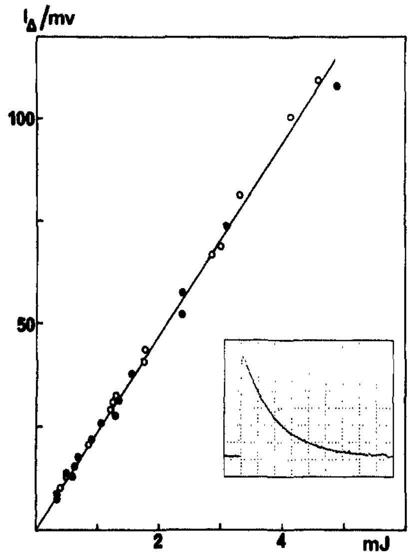

Figure 8. Emission intensity at 1270 nm extrapolated to time zero, I_Δ, against laser energy for oxygenated water-d_2 solutions of SDS (0.5 mol L^{-1}) containing BP (6 × 10^{-3} mol L^{-1}) and N (○) or B (●) (8 × 10^{-3} mol L^{-1}). Inset: Corresponding time dependence of emission at 1270 nm after absorption of a 4.2-mJ pulse by a solution containing N; 20 mV/division, 20 μs/division.

Determination of $O_2(^1\Delta_g)$ Yields. It was found possible to solubilize N and B ($\leqslant 10^{-2}$ mol L^{-1}) in SDS in water, BP being significantly more soluble. Laser excitation of BP (3–6 × 10^{-3} mol L^{-1}; OD_{355} = 0.25–0.50) in aqueous SDS (0.2–0.5 mol L^{-1}) containing N or B (0.2–1.0 × 10^{-2} mol L^{-1}) led to formation of the corresponding hydrocarbon triplets which exhibited absorption spectra (Figure 7a) essentially identical with those in cyclohexane, and the initial yields were the same in oxygenated and deoxygenated solution. The respective lifetimes, for example, 319 ns and 13.6 μs for the shorter lived $^3B^*$, showed that virtually all triplets were scavenged in oxygen-saturated solution. This was not the case in aerated solution. Because of the short lifetime of $O_2(^1\Delta_g)$ in water (4.4 μs),[7f] the infrared luminescence experiments were performed with water-d_2-based micelles for greater accuracy.[23] Thus, oxygenated water-d_2 solutions of BP (3–6 × 10^{-3} mol L^{-1}) and SDS (0.2–0.5 mol L^{-1}) containing N or B (0.2–1.0 × 10^{-2} mol L^{-1}) were subjected to pulsed laser excitation at 355 nm. In all cases $O_2(^1\Delta_g)$ emission was observed (Figure 8, inset) and decayed exponentially with a lifetime dependent on SDS concentration (vide infra). Plots of I_Δ vs. laser intensity (Figure 8) were linear and passed through the origin for energies up to ~4 mJ/pulse; results were identical for both hydrocarbons. This appears a clear indication that S_Δ = 1.0 for both $^3N^*$ and $^3B^*$ within the aliphatic interior of the micelles.

We have again performed DPBF bleaching experiments to support the above conclusion. The procedure was essentially as

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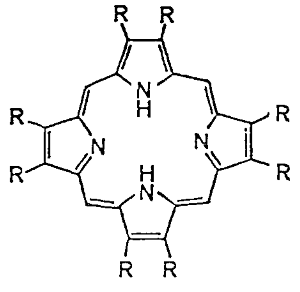
(23) The use of water-d_2 obviates the problem of errors resulting from too similar time constants for $O_2(^1\Delta_g)$ formation and decay.

for cyclohexane and benzene and was made possible by the high solubility of BP in the micellar system. This allowed essentially exclusive excitation of BP (2.4×10^{-2} mol L^{-1}; $OD_{355} = 2.0$) in oxygenated water-d_2-based micelles containing N (10^{-2} mol L^{-1}) both with and without the presence of DPBF (5×10^{-5} mol L^{-1}). As already noted, the $^3N^*$ optical density extrapolated to time zero was independent of oxygen concentration. In the DPBF bleaching experiment the DPBF occupied <2% of the micelles and did not significantly quench $^3N^*$, the lifetime of the latter being identical (72 μs) in nitrogen-purged solutions with and without DPBF. Conditions were such that eq 11 held, and determination of S_Δ in the usual way[24] yielded a value of 1.03 ± 0.15, in excellent agreement with previous conclusions in this section.

Assuming that BP and N or B occupancies of micelles are independent of each other, a Poisson treatment of occupancy probabilities[25] shows that for 0.2 mol L^{-1} SDS (critical micelle concentration 7.0×10^{-3} mol L^{-1},[26] aggregation number 65[27]) containing BP (3×10^{-3} mol L^{-1}) and N or B (10^{-2} mol L^{-1}), >96% of BP-occupied micelles will also contain one or more molecules of aromatic hydrocarbon. Thus, intramicellar energy transfer would be expected to result in essentially quantitative production of aromatic hydrocarbon triplets as a consequence of laser excitation of BP. This was confirmed by the plot in Figure 7b of $^3N^*$ and $^3B^*$ optical densities, extrapolated to time zero, as a function of N and B concentrations at an even higher SDS concentration of 0.5 mol L^{-1}. Thus oxygenated solutions of BP and N or B (10^{-2} mol L^{-1}) solubilized in SDS (0.2 mol L^{-1}) in water-d_2 produce $O_2(^1\Delta_g)$ with unit efficiency when subjected to 355-nm excitation.

Variation of τ_Δ and k_r with SDS Concentration in Water-d_2. In the previous section it was shown that, as in cyclohexane, the S_Δ value for $^3N^*$ in the interior of an SDS micelle is unity. In order to use this system as a standard for water-soluble sensitizers it was necessary to quantify the effect of the SDS micelles on $O_2(^1\Delta_g)$ properties and in particular on the efficiency of the infrared luminescence process. To do so a sensitizer was required which, in the presence of SDS, is confined to the aqueous regions of the system. In such a situation its photophysical properties, in particular ϕ_T and S_Δ, should be constant, and changes in the $O_2(^1\Delta_g)$ emission intensity will reflect changes in the rate constant, k_r, of the light-emitting process. The sensitizer chosen was uroporphyrin I (**1**; UP) which contains eight carboxylic acid residues



1, R = $CH_2CH_2CO_2H$

and whose visible electronic absorption spectrum in water is totally unchanged by addition of up to 0.5 mol L^{-1} SDS. Thus water-d_2 solutions of UP ($OD_{532} = 0.2$) containing various SDS concentrations (0–0.5 mol L^{-1}) were subjected to pulsed laser excitation at 532 nm. Both τ_Δ and I_Δ were dependent on SDS concentration. The first-order constant for decay, k_d, was essentially linear with respect to [SDS] (Figure 9a) and corresponded to lifetime, τ_Δ, changes from 68.5 μs in pure water-d_2[28] to 42.6 μs in the presence of 0.5 mol L^{-1} SDS. This change is within 10% of that calculated on the basis of micelle volume fraction considerations.[29] Plots of I_Δ vs. [SDS] were also essentially linear (Figure 9b), emission intensity increasing with [SDS] from that in pure water-d_2 by a factor of 1.0 + 2.4[SDS] L mol^{-1} which was independent of laser intensity[30] to ±3%. Thus, use of the oxygenated BP/N/SDS/water-d_2 system with 0.2 mol L^{-1} SDS, $\phi_\Delta = \phi_T = S_\Delta = 1.0$, as an absolute standard for ϕ_Δ for sensitizers solubilized in water-d_2 simply requires application of a correction factor of 1.5 ± 0.2.

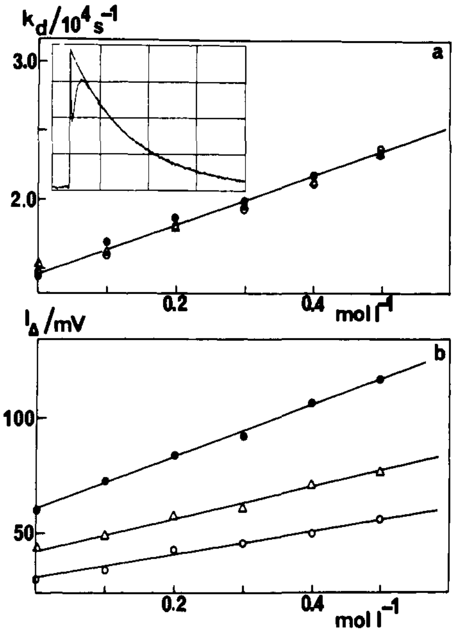


Figure 9. (a) First-order constant for decay of $O_2(^1\Delta_g)$ in aerated SDS/water-d_2 as a function of SDS concentration, sensitization by UP ($OD_{532} = 0.2$) at laser energies of 16 (●), 8 (△), and 5 (○) mJ/pulse. (b) Emission intensity extrapolated to time zero, I_Δ, against SDS concentration for the same experiments. Inset: Corresponding time dependence of emission at 1270 nm after absorption of an 8.0-mJ pulse by UP ($OD_{532} = 0.2$) in aerated water-d_2 containing SDS (0.1 mol L^{-1}); 13 mV/division, 50 μs/division; τ_Δ = 61.5 μs.

Table I. Solvent Dependence of Relative Radiative Rate Constants of $O_2(^1\Delta_g)$, k_r, and Dielectric Constants ϵ

solvent	I_Δ, mV	k_r, s^{-1}	ϵ[a]
cyclohexane	13.1	4.1	2.02
dioxane	9.5	3.0	2.21
benzene	41.6[b]	13.0	2.28
acetonitrile	8.3	2.6	37.5[d]
water-d_2	3.2[c]	1.0	79.8

[a] Reference 32 unless otherwise stated. [b] Corrected for S_Δ of 0.55. [c] Corrected for effect of SDS concentration on k_r, cf. Figure 9. [d] Reference 15.

3.3. Medium Effects on S_Δ and k_r. Although the work outlined here clearly shows that for non-benzenoid environments the efficiency of $O_2(^1\Delta_g)$ formation from N, B, and F triplets is unity, we have no explanation for the anomalous behavior in benzenoid media; analysis shows that the reason does not lie with differences in standard solvent physical properties: viscosity, dielectric constant, etc. It is well-known that oxygenated organic solvents may

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[24] The extinction coefficient of $^3N^*$ in SDS at 415 nm, ϵ_{415}, was determined by direct comparison of optical densities at this wavelength extrapolated to time zero after laser excitation of optically matched solutions of BP ($OD_{355} = 0.5$) and N (10^{-2} mol L^{-1}) in (a) deaerated water containing SDS (0.5 mol L^{-1}) and (b) deaerated cyclohexane, ϵ_{415} = 24 500.[21]

[25] Dorrance, R. C.; Hunter, T. F. *Trans Faraday Soc.* **1972**, *68*, 312. Rodgers, M. A. J.; da Silva e Wheeler, M. F. *Chem. Phys. Lett.* **1978**, *53*, 165.

[26] Turro, N. J.; Lee, P. C. C. *J. Phys. Chem.* **1982**, *86*, 3367.

[27] Llanos, P.; Lang, J.; Strazielle, C.; Zana, R. *J. Phys. Chem.* **1982**, *86*, 1019.

[28] This lifetime is essentially identical with a recently published value of 68.1 ± 2.5 μs for water-d_2.[7g]

[29] Lee, P. C.; Rodgers, M. A. J. *J. Phys. Chem.* **1983**, *87*, 4894.

[30] The longer time constant for $O_2(^1\Delta_g)$ formation in these experiments (cf. Figure 9a, inset) is due to the relatively low oxygen concentration (2.2×10^{-4} mol L^{-1}) in aerated water. This did not influence the accuracy of the extrapolation procedure, partly because of the relatively long τ_Δ, 42–69 μs, in these experiments. This was confirmed when plots of I_Δ vs. laser energy (5–20 mJ/pulse) for aerated and oxygenated solutions of SDS (0.5 mol L^{-1}) in water-d_2 containing UP ($OD_{532} = 0.28$) gave essentially identical results.

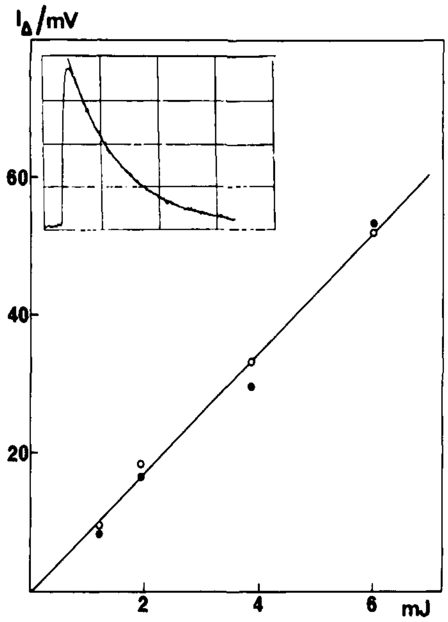

Figure 10. Emission intensity at 1270 nm extrapolated to time zero, I_Δ, against laser energy for aerated dioxane solutions of *p*-MAP (OD_{355} = 0.53) containing N (○) or F (●) (10^{-1} mol L^{-1}). Inset: Corresponding time dependence of emission at 1270 nm after absorption of a 6.0-mJ pulse by a solution containing N; 12 mV/division, 30 μs/division; τ_Δ = 26.6 μs.

exhibit additional electronic absorption at wavelengths longer than in deaerated medium,[31] and it has been demonstrated[31e] that this effect is due to contact charge-transfer interaction between solvent and oxygen as the electron acceptor, although no stable complexes are formed. A reasonable correlation between solvent IP and extended absorption characteristics was found.[31e] We have therefore examined $O_2(^1\Delta_g)$ emission intensities in dioxane on the grounds that this solvent (a) is non-benzenoid, (b) is closest to benzene, of the common solvents previously examined,[31e] in terms of IP/contact CT absorption characteristics, and (c) has a reasonably long τ_Δ (26 μs). In Figure 10 are shown I_Δ vs. laser intensity plots resulting from *p*-MAP sensitization of $^3N^*$ and $^3F^*$ formation in aerated dioxane. In the light of previous results the identical slopes are a clear indication that, in contrast to benzene (Figure 3a), S_Δ is unity in each case. Solvent–oxygen interaction does not therefore appear to provide an explanation of the anomalous behavior in benzenoid media.

In Table I are shown relative $O_2(^1\Delta_g)$ emission rate constants, k_r, for cyclohexane, dioxane, benzene, acetonitrile, and water-d_2. The numbers are calculated from the I_Δ values in mV for experiments carried out under identical conditions in a single experimental session such that, as already demonstrated in sections 3.1 and 3.2, equal concentrations of $^3N^*$ were produced and efficiently scavenged by oxygen. The values for benzene and water-d_2 have been corrected respectively for an S_Δ value of 0.55 (section 3.1) and the effect of SDS concentration on k_r (section 3.2). Yet again benzene appears to behave anomalously in that for the other four media k_r decreases with dielectric constant, albeit only by a factor of 4. This contrasts mildly with the conclusions of Krasnovskii[33] that k_r is independent of solvent.

4. Conclusions

The oxygen quenchings of simple aromatic hydrocarbon triplets, produced with unit efficiency by energy transfer from the triplets of aromatic ketones excited at 355 nm, yield identical amounts of singlet oxygen, $O_2(^1\Delta_g)$, as determined by time-resolved infrared emission spectroscopy in non-benzenoid media, namely, cyclohexane, dioxane, acetonitrile, and SDS micelles in water-d_2. The clear indication that the efficiency of $O_2(^1\Delta_g)$ formation, S_Δ, is unity in each case has been confirmed by DPBF bleaching experiments for cyclohexane and SDS micelles. In contrast, similar experiments for benzene and toluene show that S_Δ varies significantly from one hydrocarbon to another. This has also been confirmed by DPBF bleaching experiments. Although the reason for this difference is not understood it seems likely that solvent–sensitizer as opposed to solvent–oxygen interactions are likely to be responsible. As a standard for $O_2(^1\Delta_g)$ formation quantum yields, ϕ_Δ, N is the preferred hydrocarbon component for each system in that the relatively weak absorption of its triplet at 355 nm is likely to extend the linearity of its response to laser energy, clearly of possible importance when examining sensitizers of low overall efficiency. A comparison of the UP-sensitized emission intensities as a function of SDS concentration in water-d_2 has provided a correction factor for the effect of SDS on the radiative rate constant, k_r. This allows the use of the oxygenated BP/N/SDS/water-d_2 system as a direct comparative standard for measuring overall quantum yields, ϕ_Δ, for water-soluble sensitizers which absorb at 355 nm.

Acknowledgment. Experiments were performed at the Christie Hospital and Holt Radium Institute, Manchester, and the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is jointly supported by NIH Grant RR00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas at Austin. Support for this work came from SERC Grant GR/D 52169 (A.A.G.) and NIH Grant GM24235 (M.A.J.R.).

Registry No. Naphthalene, 91-20-3; biphenyl, 92-52-4; fluorene, 86-73-7; O_2, 7782-44-7.

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