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Chemistry of Singlet Oxygen. 42. Effect of Solvent, Solvent Isotopic Substitution, and Temperature on the Lifetime of Singlet Molecular Oxygen ($^1\Delta_g$)

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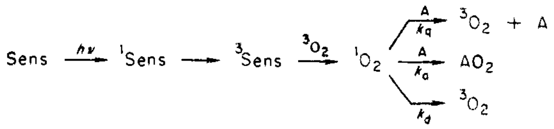
Abstract: The deactivation by solvent molecules of the lowest excited singlet state of molecular oxygen ($^1\Delta_g$) to its ground state ($^3\Sigma_g^-$) is discussed. Solvent deuterium isotope effects on the lifetime of singlet oxygen have been determined for various solvents. Several spectroscopic and chemical techniques were employed, including time-resolved direct observation of $^1O_2(^1\Delta_g)$ luminescence at 1270 nm. Currently accepted explanations for the effect of environment on the lifetime of singlet oxygen are simplifications of a very complex problem. The problem is defined, stressing points central to the energy-transfer process which have been neglected in the past.

In recent years it has become increasingly evident that the lifetime of singlet molecular oxygen ($^1\Delta_g$) is solvent dependent.[1-17] The lifetime may differ by a factor of several hundred in common organic solvents. The usual methods of determining the lifetime of singlet oxygen in solution are indirect and involve monitoring the loss of a molecule (A) which reacts with singlet oxygen, generated by energy transfer from a triplet sensitizer (Scheme I).[1,14,15] The kinetics involved in all of these techniques, however, are often complicated and require that several experimental conditions be met. In a preliminary communication,[17] we reported solvent deuterium isotope effects on the lifetime of singlet oxygen ($^1\Delta_g$) determined using steady-state techniques. Our results suggested that published values of singlet oxygen lifetimes, particularly those in deuterated solvents, were in need of critical reevaluation. In a subsequent communication,[18] we reported values for k_d in various solvents determined by time-resolved studies of singlet oxygen luminescence at 1270 nm. It was shown that lifetime values determined using the indirect techniques mentioned above are often inaccurate and tend to be somewhat low, particularly when $\tau(^1O_2)$ is large. In this case, there are inherent limitations in the indirect approaches which preclude accurate determination of $\tau(^1O_2)$ except by the direct method.

Scheme I



The lack of reliable values for the lifetime of singlet oxygen in various solvents has made the development of an acceptable theory for the interaction between solvent molecules and singlet oxygen difficult. Kearns and Merkel[5] provided the most reasonable explanation for the effect of solvent on k_d using the values available at the time. They presented an empirical expression relating the rate constant for decay of singlet oxygen to a linear combination of values of solvent optical densities in regions coincident with electronic transitions of the oxygen molecule. Since these transitions occur in the near-infrared and overlap with solvent overtones and combinations of C–H and OH vibrational modes, they suggested that electronic-to-vibrational energy transfer was responsible for the deactivation of $^1O_2$. A summary of results published in preliminary form, some previously unpublished quenching experiments, and studies of the temperature effect on $\tau(^1O_2)$ are presented in part I of this paper. Part II is a critical discussion of the mechanism of quenching of singlet oxygen ($^1\Delta_g$) by solvents. The problem is shown to be a complex one which cannot be explained by a simple correlation of the sort developed by Kearns, although electronic-to-vibrational energy transfer is certainly a key factor.

I. Lifetime of Singlet Oxygen ($^1\Delta_g$) in Solution

1. Isotope Effects. The usual kinetic scheme for reactions of singlet oxygen is used, in which an acceptor (A) quenches (k_q) or reacts with (k_a) singlet oxygen generated by energy transfer from a sensitizer in its triplet state (Scheme I).[17] Using the usual steady-state treatment and adjusting the concentration of the acceptor A such that the rate constant for the decay of singlet oxygen (k_d) is much larger than $(k_a + k_q)[A]$, the disappearance of the acceptor is expressed by

$$\ln \frac{[A]}{[A]_0} = -K\frac{k_a}{k_d}t = k_{obsd}t \qquad (1)$$

K is the rate constant for formation of singlet oxygen, which includes the rate of light absorption by the sensitizer, the quantum yield of intersystem crossing of the sensitizer, and the fraction of triplet sensitizer quenched by ground-state oxygen.

It was shown[17] that for rubrene and 1,3-diphenylisobenzofuran (DPBF), first-order plots of the fluorescence of acceptor vs. time (Young's technique[2]) are linear with a slope of k_{obsd}. K was

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Table I. Lifetime of Singlet Molecular Oxygen ($^1\Delta_g$) in Solution (μs)

solvent	lit. values, determined by indirect techniques	lit. values, determined by direct techniques	this work
acetone-h_6	26.3 ± 7.0,[a] 42.0 ± 8.0,[c] 55.0 ± 1.3[f]	50,[j] 51 ± 5,[q] 51,[g] 40,[h] 39,[i] 51[r]	46.5 ± 2.0
acetone-d_6	602–1042,[f] 26[b]	640,[g] 588[r]	690 ± 20
acetonitrile-h_3	30.3 ± 6.8,[b] 57.0 ± 9.0,[c] 92 ± 5[f]	61,[h] 68,[i] 69[r]	54.4 ± 1.3
acetonitrile-d_3	885–2128[f]	440,[h] 621[r]	600 ± 33
benzene-h_6	23.8 ± 6.5,[b] 27 ± 4,[c] 24.4 ± 2.4,[l] 25.6 ± 2.5,[n] 28.2 ± 0.4[f]	30 ± 4,[q] 32,[g] 28[r]	26.7 ± 1.3
benzene-d_6	36.0 ± 7.0,[m] 740–1540,[f] 500–1000[f]	700,[g] 628[r]	550 ± 11
D_2O	33.3 ± 2.1,[o] 35.7 ± 2.0,[o] 53 ± 5,[d] 42 ± 5,[p] 53 ± 3,[e] 120[k]	100,[j] 58,[i] 55[r]	68.1 ± 2.5

[a] Reference 6. [b] References 5 and 6. [c] Reference 19. [d] Reference 38. [e] Reference 39. [f] Reference 40, maximum range of values reported. [g] Reference 41. [h] Reference 41; rose bengal was sensitizer. [i] Reference 41; methylene blue was sensitizer. [j] References 42 and 43. [k] Reference 43. [l] Reference 44. [m] Reference 1. [n] Reference 15. [o] Reference 45. [p] Reference 46. [q] References 34 and 37. [r] Reference 48.

experimentally determined to be invariant to solvent deuteration.[17] With the reasonable assumption that k_a likewise does not change appreciably on solvent deuteration, changes in the value of k_{obsd} were attributed to changes in $\tau(^1O_2)$.[17] The ratio of k_{obsd} for experiments in protiated and deuterated solvents, therefore, yield the solvent deuterium isotope effect on $\tau(^1O_2)$. The results of this study suggested that the previously reported values for $\tau(^1O_2)$ in both acetone-d_6 and benzene-d_6 (26 and 36 ± 7 μs, respectively)[1,5,6,19] were in error, since the measured isotope effects for acetone (~18) and benzene (~16) would predict actual singlet oxygen lifetimes in the deuterated solvents on the order of 500–600 μs (assuming the reported values for the lifetimes in protiated solvents were correct).

It has long been recognized that for solvents in which the singlet oxygen lifetime is long, the indirect methods for determining it cannot be used with accuracy.[3] In the original approach taken by Wilkinson,[14] it is easily shown that for lifetimes significantly larger than 10–15 μs, the kinetics become quite complicated and that errors may result. In the variation to the technique introduced by Young[3] this point is carefully addressed, and the approximate limits of reliability of the technique are defined. From Young's analysis, it follows that for lifetimes larger than ~100 μs, the indirect methods may result in values of $\tau(^1O_2)$ which are far from accurate. To avoid these problems, values of $\tau(^1O_2)$ were determined in various solvents by direct observation of singlet oxygen phosphorescence at 1270 nm following pulsed laser excitation of a sensitizer.[18]

2. Luminescence Experiments. Luminescence from $^1O_2(^1\Delta_g(v = 0) \rightarrow {}^3\Sigma_g^-(v = 0))$ at 1270 nm has been observed for some time from the upper atmosphere[20–24] and in gas-phase reactions.[25–31] The first reported observations of this phosphorescence in solution were made by Krasnovskii[32] and then by Kasha and Khan[33] using steady-state techniques. Studies of the luminescence after flash excitation of sensitizing dyes by Byteva et al. quickly followed.[34–37]

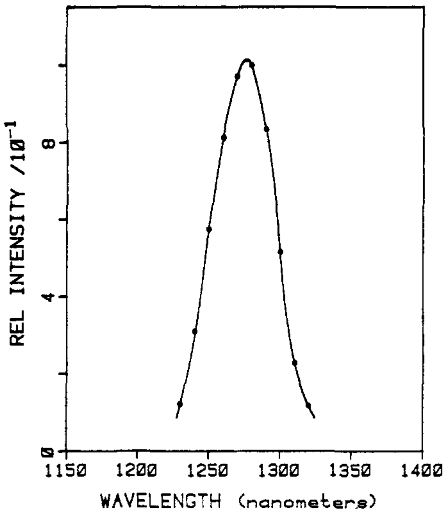

Figure 1. Emission spectrum of singlet oxygen ($^1\Delta_g$) in solution (acetone-h_6). Mesoporphyrin IX dimethyl ester was used as sensitizer.

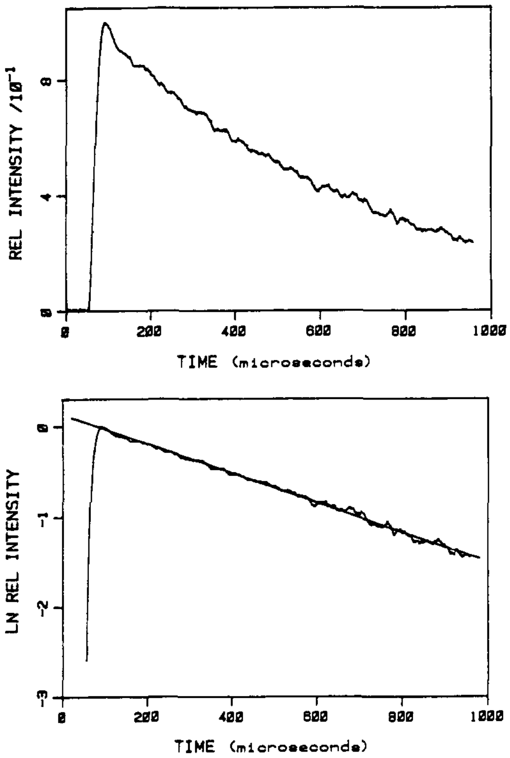

Figure 2. (a) Exponential decay of singlet oxygen luminescence at 1270 nm in acetone-d_6 (top). (b) First-order plot of the data (bottom).

The experimental approach used in our investigations is similar to that of the Russian workers (see the Experimental Sections for Details). A sensitizing dye, excited with a pulsed laser beam (4-ns

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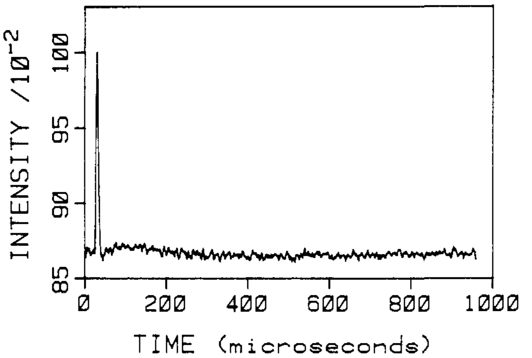

Figure 3. Luminescence from an oxygenated solution of acetone-d_6 after the addition of an excess of tetramethylethylene (TME). The peak at approximately 40 μs is a result of scattered light and rf noise from the laser flash. Singlet oxygen luminescence is shown to be efficiently quenched.

peak width at half-height), transfers energy to oxygen from its triplet state to give singlet molecular oxygen ($^1\Delta_g$). Luminescence at 1270 nm was detected by an intrinsic germanium photodiode and characterized as that of singlet oxygen by its emission spectrum (Figure 1), by quantitative quenching studies using 2,3-dimethyl-2-butene and 1,4-diazabicyclo[2.2.2]octane (Dabco), and by the decrease in luminescence intensity when an interference filter centered at 1270 nm was replaced by one centered at 1300 nm. The λ_{max} of the emission spectrum (~1277 nm, uncalibrated) was slightly red shifted from values reported elsewhere.[33]

Several dyes were used to allow sufficient solubility in the various solvents. For most of the work, mesoporphyrin IX dimethyl ester was used. *meso*-Tetraphenylporphine, 1,8-dinaphthalenethiophene, rose bengal, and thionine hydrochloride were also used, the latter two in D_2O.

Since singlet oxygen is formed essentially instantaneously on a microsecond timescale, its decay should follow simple first-order kinetics. A representative decay trace of the 1270 nm luminescence is shown in Figure 2a. Semilogarithmic plots of the data are linear (Figure 2b), confirming the kinetic suppositions, and directly yield the lifetime of singlet oxygen. On addition of excess tetramethylethylene (TME) to the solutions, singlet oxygen is efficiently removed (Figure 3). Table I lists values for the lifetime of singlet oxygen determined by this technique along with values reported by other investigators. For the solvents in which several different dyes were used, differences in the observed lifetimes did not exceed the limit of error inherent in this technique. Lifetime values that have been determined by indirect time-resolved methods are also reported in Table I.

Using the observed values for the lifetime of singlet oxygen in protiated and deuterated solvents, values for the solvent isotope effect were calculated and are compared with the values independently determined using steady-state techniques in Table II. Similar ratios calculated from recent results of Hurst, McDonald, and Schuster,[41] and of Parker and Stanbro[47] (direct observations of $^1O_2$ luminescence) and Rodgers[40] (indirect time-resolved study) are included. Additional values reported since this work was completed by Rodgers[48] and by Turro[49] are also included. Agreement between the values is as good as can be expected, considering the limitations of the indirect technique.

Table II. Solvent Deuterium Isotope Effects on the Lifetime of Singlet Molecular Oxygen ($^1\Delta_g$); $k^H{}_{decay}/k^D{}_{decay}$

	from time-resolved direct observation of 1.27-μ luminescence		from steady-state studies	
solvent	this work[a]	literature	this work[b]	literature
acetone	14.8 ± 1.1	12.5 ± 2.5[c]	19.9 ± 1.3	
		15 ± 3[d]	17.0 ± 3.8	13.8 ± 4.0[f]
		12.8 ± 2.9[h]	17.8 ± 2.0	19.7 ± 3[g]
		11.5[i]		
acetonitrile	11.0 ± 0.9	7.2 ± 1.4[e]	8.7 ± 1.0	13.4 ± 6.0[f]
		9.0[i]	7.2 ± 1.6	16.4 ± 2[g]
benzene	20.6 ± 1.4	21.9 ± 4.4	15.9 ± 2.1[j]	35 ± 13[f]
		22.4[i]	16.8 ± 1.0	27.2 ± 1[g]

[a] Calculated from values shown in Table I. [b] Reference 17. [c] Reference 41; *meso*-tetraphenylporphine was the sensitizer. [d] Reference 41; calculated using an average of values reported for k_d (acetone-h_6). [e] Reference 41; rose bengal was the sensitizer. [f] Reference 40. [g] Reference 49; determined from steady-state luminescence at 1.27 μ. [h] Reference 47. [i] Reference 48. [j] Contained 0.8% (by volume) CH_3OH in order to dissolve methylene blue. Using the pulsed laser technique, additiun of a comparable amount of CH_3OH to the system shortens the lifetime of singlet oxygen in benzene-d_6 sufficiently to yield an isotope effect of approximately 16. The expected isotope effect, calculated using a value of $\tau(^1O_2)$ in CH_3OH of 10 μs (ref 1, 50) is 15.

Table III. Quenching of Singlet Oxygen by Dye Molecules. Values of k_d for Singlet Oxygen and $(k_a + k_q)$ for Dye Molecules Determined from Plots of α vs. [Q][a]

solvent	av laser energy (joules/pulse)	$(k_a + k_q)^b$ (s^{-1} M^{-1})	$\tau(^1O_2)^c$ (μs)	$\tau(^1O_2)$ from Table I
acetone-h_6	0.004	$(3.8 \pm 1.2) \times 10^7$ [d]	42.7 ± 1.0	46.5 ± 2.0
acetone-d_6	0.004	$(1.0 \pm 0.5) \times 10^7$ [d]	760 ± 60	690 ± 20
CH_3CN	0.011	2.5×10^7 [d]	54.6	54.4 ± 1.3
CD_3CN	0.004	2.2×10^7 [d]	670 ± 60	600 ± 33
benzene-h_6	0.011	$(6.4 \pm 2.1) \times 10^7$ [e]	27.4 ± 1.4	26.7 ± 1.3
D_2O	0.004	$(6.8 \pm 0.5) \times 10^7$ [f]	78.8 ± 3.0	68.1 ± 2.5
D_2O	0.011	6.3×10^7 [f]	65.8	

[a] $\alpha = k_d + (k_a + k_q)[Q]$, the observed rate constant for singlet oxygen decay in the presence of a quencher (see section 4). [b] Slope of the plot of α vs. [Q], the rate constant for quenching of $^1O_2$ by the dye. [c] Reciprocal of the intercept of the plot of α vs. [Q]. [d] Mesoporphyrin IX dimethyl ester. [e] *meso*-Tetraphenylporphine. [f] Thionine hydrochloride.

3. Effect of Sensitizer Concentration and Laser Power on the Lifetime of Singlet Oxygen. In the course of this work, it was discovered that high sensitizer concentrations or high laser powers can yield lifetimes which are lower than those measured under other conditions. This effect is particularly important for solvents in which the lifetime of singlet oxygen is long. Using values for the lifetime of singlet oxygen determined at high dye concentrations or at high laser powers, one can extrapolate to obtain corresponding values at low concentrations and powers (Table III).[51] Despite the inherent error in the extrapolated values, the results agree reasonably well with the numbers reported in Table I and show that the corrections for this quenching are minor under our conditions.

The calculated rate constant for quenching of singlet oxygen by mesoporphyrin IX dimethyl ester (~2.0×10^7 s^{-1} M^{-1} in both acetonitrile and acetone) is an order of magnitude higher than the value reported by Krasnovskii (2.0×10^6 s^{-1} M^{-1} in CCl_4),[42,54] and also significantly larger than those reported by Whitten.[55]

The quenching of singlet oxygen by porphyrins has been discussed in the literature.[42,52-55] The reasons for our larger values

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are not entirely clear, but there may be processes in addition to quenching by ground-state porphyrins which need to be considered at the high power densities used here. For the porphyrins it is known that ionization potentials are low and that Rydberg states are readily populated.[56,57] It is also reported that the extinction coefficient of the triplet state of several porphyrins far exceeds that of the ground state at 530 nm, the wavelength used to excite these dyes.[57] Thus, even though quenching of the triplet by O_2 is fast, photolysis of triplet is possible at high power levels. Ejection of electrons from aromatic molecules of low ionization potential is well documented.[58] Consequently, the following process would produce $O_2^{-}\cdot$, a powerful quencher of singlet oxygen.[59–60]

$$^3\mathrm{Sens} \xrightarrow{h\nu} (^3\mathrm{Sens})^* \xrightarrow{h\nu} \mathrm{Sens}^{+}\cdot + e^- \xrightarrow{^3O_2} O_2^{-}\cdot$$

$$O_2^{-}\cdot + {}^1O_2 \rightarrow {}^3O_2 + O_2^{-}\cdot$$

Koizumi has shown that in aqueous and alcoholic media, the interaction of an excited triplet-state sensitizer with a ground-state sensitizer (D–D interaction) can lead to a radical ion pair ($\mathrm{Sens}^{+}\cdot$ + $\mathrm{Sens}^{-}\cdot$).[61–64] This process becomes particularly efficient at high sensitizer concentration. The ion pair is efficiently attacked by oxygen to give superoxide ion ($O_2^{-}\cdot$).

$$\begin{tikzcd} {^3\mathrm{Sens} + \mathrm{Sens}} \arrow[r] & {(\mathrm{Sens}^{+}\cdot + \mathrm{Sens}^{-}\cdot)} \arrow[d, "O_2"] \\ & {\mathrm{Sens} + \mathrm{Sens}^{+}\cdot + O_2^{-}\cdot} \end{tikzcd}$$

It was suggested by Koizumi that the quantum yield for the formation of ($\mathrm{Sens}^{+}\cdot$ + $\mathrm{Sens}^{-}\cdot$) can be larger than 10^{-2}. Koizumi also suggested that oxidative bleaching of a dye molecule occurs primarily through the intermediate ($\mathrm{Sens}^{+}\cdot$ + $O_2^{-}\cdot$) rather than through photooxygenation by $^1O_2$.

A third process to be considered is the interaction of a triplet dye molecule with singlet oxygen, shown by Kearns to deactivate singlet oxygen in the gas phase.[65] This process can be important only at high laser power levels.

Photooxygenated dye molecules also appear to quench singlet oxygen. In some cases, solutions could only be used once (signal averaging 64 to 128 pulses); subsequent lifetime determinations yielded values for $\tau(^1O_2)$ successively lower than previous values. Absorption spectra of dyes taken after irradiation show changes. In some cases (1,8-dinaphthalenethiophene, thionine hydrochloride, and zinc tetraphenylporphine), extensive bleaching occurred. Mesoporphyrin IX dimethyl ester is photooxygenated to yield a compound which has an absorption at 650 nm with negligible changes in the spectrum at other respectively. For solvents in which the lifetime of singlet oxygen is long, dye destruction is particularly noticeable. Extensive reaction of the dyes occurred upon photolysis in $CHCl_3$ and CCl_4. In a previous communication,[17] it was shown that species other than singlet oxygen (perhaps radical reactions) complicate photooxygenation reactions in chloroform. It does not seem unreasonable that these complications would be compounded under laser flash conditions, where light intensities are high.

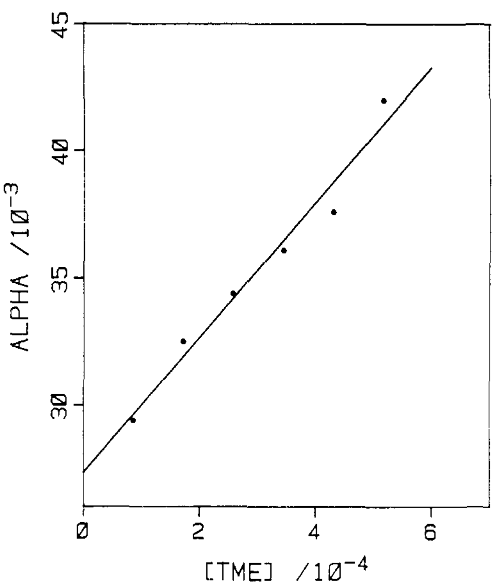

Figure 4. The quenching of singlet oxygen by tetramethylethylene (TME). The plot of α vs. [TME] has a slope of (k_a + k_q) for the reaction of TME with singlet oxygen and an intercept of k_d. α is the observed rate constant for the decay of singlet oxygen in the presence of a quencher.

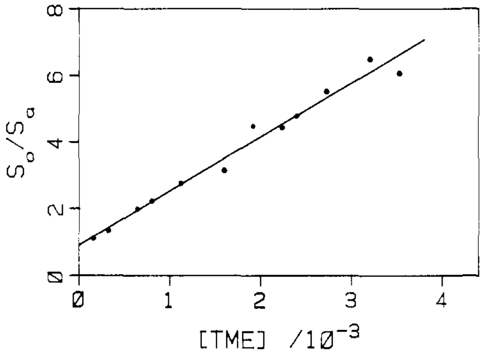

Figure 5. Stern–Volmer plot determined according to Young's technique[2] for tetramethylethylene (TME) in acetone-h_6 at +21 °C. Resultant β value is (6.3 ± 1.0) × 10^{-4} M.

4. Quenching Studies: Tetramethylethylene (TME) and Dabco. A series of experiments was carried out in which the lifetime of singlet oxygen was decreased by reaction with 2,3-dimethyl-2-butene (TME) and quenching by 1,4-diazabicyclo[2.2.2]octane (Dabco). Under conditions where the concentration of A changes negligibly over the reaction period, first-order kinetics result, with an observed rate constant for decay of singlet oxygen of α ($\alpha = k_d + (k_a + k_q)[A]$). The slope and intercept of a plot of α vs. [A] give values of (k_a + k_q) for the inhibitor and k_d for the solvent, respectively.

For the experiments in which TME was the inhibitor, minimal photooxygenation of the olefin occurred. The samples were prepared under red light and singlet oxygen lifetimes were determined by averaging only 32 indpendent decay traces (32 successive laser flashes). Under these conditions the concentration of unreacted substrate (A) remained nearly constant over the period of photolysis. Consequently, the kinetic assumptions are valid. Also, quenching of singlet oxygen by product hydroperoxide (less reactive than olefin) is unimportant. The plot obtained is shown in Figure 4.

Analysis of the data yields a lifetime of $^1O_2$ in acetone-h_6 of 37 ± 3 μs which corresponds extremely well with values (37 μs) independently determined at the dye concentrations used in this experiment (1 × 10^{-4} M). The rate constant for reaction of TME with singlet oxygen (k_a + k_q) was determined to be (2.7 ± 0.6) × 10^7 M^{-1} s^{-1}. Wilkinson reports[16] a "preferred value" for (k_a + k_q) based on 36 independent experiments of (3.0 ± 1.3) × 10^7

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Table IV. Effect of Temperature on the Lifetime of Singlet Oxygen in Acetone-h_6

temp (°C)	τ (μs)	temp (°C)	τ (μs)
+21.5	47.3 ± 1.0	−60.0	47.7 ± 0.4
−16.0	47.6 ± 1.0	−81.3	50.3 ± 1.0
−37.6	48.0 ± 1.1		

M^{-1} s^{-1}. The β value calculated using ($k_a + k_q$) and the value of k_d reported in Table I is (8 ± 2) × 10^{-4} M. Using Young's technique,[2] an independent determination of β for TME in acetone-h_6 gave a value of (6.3 ± 1.0) × 10^{-4} M (the Stern–Volmer plot for this experiment is shown in Figure 5). Both of these values agree with a literature value of (7.2 ± 0.2) × 10^{-4} M.[16,66]

A similar treatment of the Dabco data results in a lifetime value of singlet oxygen in acetone of 41.8 ± 5.8 μs and a quenching rate constant ($k_a + k_q$) of (4.5 ± 0.5) × 10^8 M^{-1} s^{-1}. Quenching rate constants reported in the literature include 15.0 and 8.1 × 10^6 M^{-1} s^{-1} (MeOH),[11,67] (3.1 ± 2.0) × 10^8 M^{-1} s^{-1} (C_5H_5N),[68] and 5.2 × 10^7 M^{-1} s^{-1} ($CHCl_3$).[69] It has been established that rate constants for quenching of singlet oxygen ($^1\Delta_g$) by aliphatic amines can be correlated with the ionization potential of the amine.[69–71] Quenching proceeds by a charge-transfer interaction between singlet oxygen and the amine. The oxidation potential for Dabco in an aprotic solvent (0.66 eV vs. SCE in CH_3CN) is significantly lower than the corresponding value in a protic solvent (0.87 eV vs. SCE in MeOH).[72] Consequently, the rather large value for quenching observed in acetone is not unexpected.

5. Effect of Temperature on the Lifetime of Singlet Oxygen. The results of only three investigations on the effect of temperature on the lifetime of singlet oxygen have been published. In 1968 Koch reported that the decay constant of the oxygenating intermediate in sensitized photooxygenations ($^1O_2$) changes negligibly in MeOH over a temperature range of about 150 °C.[73] In 1975, using the indirect laser flash technique, Kearns reported a 50% decrease in the lifetime (~120 to 70 μs) on going from −50 to +25 °C in $CHCl_3$.[8] Considering the limitations of this technique and the problems known to occur in chloroform,[17] it is difficult to attribute the reported temperature effect solely to a change in $\tau(^1O_2)$. Finally, using a pulse radiolysis technique to generate singlet oxygen in toluene, Rodgers reported a ~50% decrease in $^1O_2$ lifetime (~34 to 24 μs) over the range −50 to +60 °C.[74] The technique used, however, is again one in which $\tau(^1O_2)$ is determined indirectly by following the time-resolved bleaching of DPBF.

The lifetime of singlet oxygen was determined directly in acetone-h_6 at a series of temperatures. Mesoporphyrin IX dimethyl ester (1.2 × 10^{-4} M) was used as sensitizer. The lifetimes measured by the germanium detection system are reported in Table IV. Over the 100 °C temperature range reported, negligible changes in lifetime are observed.

In a less direct measurement, β values ($k_d/(k_a + k_q)$) for tetramethylethylene (TME) were determined in acetone-h_6 using Young's steady-state technique[2] at −67 and +21.0 °C. The β value determined at −67 °C (7.7 ± 1.0 × 10^{-4} M) does not differ significantly from that determined at +21 °C (6.3 ± 1.0 × 10^{-4} M). Since k_d was shown in the time-resolved study to be temperature independent, the quantity ($k_a + k_q$) for TME must likewise change negligibly over the range studied. Stern–Volmer plots for this steady-state temperature study are shown in Figure 5 and 6.

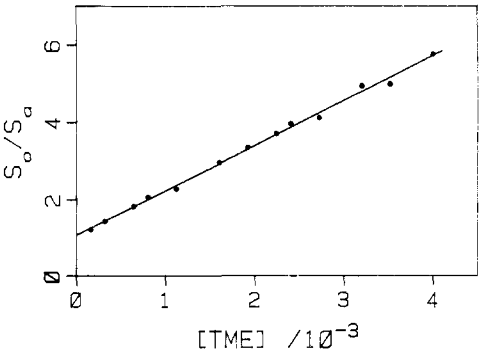

Figure 6. Stern–Volmer plot determined according to Young's technique[2] for tetramethylethylene (TME) in acetone-h_6 at −67 °C. Resultant β value is (7.7 ± 1.0) × 10^{-4} M.

II. Quenching of Singlet Molecular Oxygen ($^1\Delta_g$) by Solvent Interactions. A Theoretical Discussion

In this section, various theoretical approaches to the problem of the transfer of the electronic excitation energy of singlet oxygen ($^1\Delta_g$) to the vibrational modes of the solvent are discussed. In particular, evidence is provided which suggests that the approach taken by Kearns[5] does not adequately describe the quenching of singlet oxygen by solvent molecules.

As an electric dipole transition, the process

$$^1O_2(^1\Delta_g) \leftrightarrow {}^3O_2(^3\Sigma_g^-)$$

is forbidden on the basis of orbital angular momentum, symmetry, spin, and parity. As a magnetic dipole or quadrupole transition, however, the transition probability increases. In addition, if electronic motion is coupled to nuclear vibrations or rotations or if spin angular momentum is coupled to orbital angular momentum, the transition likewise becomes more probable.[20] These higher orrder contributions may result from either a collision or interaction with an external field. The lifetime of $^1O_2(^1\Delta_g)$ in a "collision-free" environment (e.g., the upper atmosphere) is on the order of 45 min;[21] in solution, however, the lifetime ranges from one to several hundred microseconds depending on the solvent. Since oxygen does not have as many vibrational degrees of freedom as a polyatomic solvent molecule, the medium must not only serve to induce transitions but must provide a sink for the electronic excitation energy of oxygen. Electronic transitions in molecular oxygen, therefore, are dependent on the perturbations offered by the solvent.

It is recognized that the probability of a "forbidden" transition may be increased by "stealing" intensity from an allowed transition.[75,76] For instance, as a result of electron exchange between two oxygen molecules, the induced transition ($^1\Delta_g + {}^3\Sigma_g^-$) ↔ ($^3\Sigma_g^- + {}^3\Sigma_g^-$) may steal intensity from the electric dipole allowed Schumann–Runge transition ($^3\Sigma_g^- \leftarrow {}^3\Sigma_v^-$).[77–80] Such intensity stealing may also be the result of a perturbation (e.g., vibrational-electronic coupling) that mixes zero-order wave functions, for instance, in a complex between oxygen and a solvent molecule. Given the general guidelines for state mixing, it seems reasonable that different solvents, whose excited-state energy levels are correspondingly different, will mix eigenstates of oxygen to differing extents.[76,77] The result will be that probabilities of transition from one oxygen state to another depend on solvent. In addition, there is a great deal of experimental evidence which supports the existence of a charge-transfer state between oxygen and various solvent or quenching molecules.[70,71,81–85] In particular, Ogryzlo[70,71]

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has reported a correlation between the ionization energy of various amines and the quenching rate of $^1O_2(^1\Delta_g)$. Theoretical conclusions suggest that matrix elements which couple the charge-transfer states with other states of the oxygen-solvent complex are large.[86-92] The relative importance of charge-transfer contributions to the transition probability will, likewise, vary according to the solvent.[84]

A great deal of work has been expended in examining possible correlations between rates of energy transfer and the extent of overlap between the emission and absorption profiles of the energy donor and acceptor, respectively. It has been shown both theoretically and experimentally that, in certain cases, exchange transfer between electronic and vibrational degrees of freedom is an inefficient process unless there is a near coincidence of vibrational and electronic energy levels.[93-96] These results form the background for Kearns' theory. Kearns suggested that the rate constant for energy transfer from singlet oxygen is directly correlated with the optical density of the solvent at wavelengths corresponding to transitions where oxygen is left in its ground electronic state with varying numbers of vibrational quanta. It was suggested that the relative importance of the transitions to different vibrational levels were determined by Franck–Condon factors in the oxygen molecule itself.[5] In the empirical expression introduced by Kearns for a limited number of solvents (eq 2),

$$\frac{1}{\tau_{^1O_2}} = 0.5(OD)_{0-0} + 0.05(OD)_{0-1} + \text{higher terms} \qquad (2)$$

coefficients ("Franck-Condon factors") are multiplied by values for the optical density of the solvent in regions that correspond to oxygen transitions (OD_{x-y}).

A careful attempt was made to find a correlation between the observed solvent isotope effects on singlet oxygen decay rates and the optical density of the solvent in regions that correspond to oxygen transitions. The 0–0 transition ($^1\Delta_g$ – $^3\Sigma_g^-$) of singlet oxygen occurs at 1270 nm (22.5 kcal mol^{-1} or 7874 cm^{-1}). This transition falls in the near-infrared where overtones and combinations of C–H and O–H bonds occur. The 0–1 transition of oxygen ($^3\Sigma_g^-(v = 1) \leftarrow {}^1\Delta_g(v = 0)$) has been observed both in the gas phase[24,97-99] and in solution[37,97] and occurs at 1584 nm (6314 cm^{-1}). Given this information and assuming slight anharmonicity in the ground-state potential well, the energy for the transition $^3\Sigma_g^-(v = 2) \leftarrow {}^1\Delta_g(v = 0)$ was estimated to be 4794 cm^{-1}. This value corresponds quite well to those independently calculated using more rigorous techniques.[24]

Since emission spectra indicate that the oxygen transitions may be broadened by solvent perturbations,[32,33] a more reasonable estimate of the overlap between solvent and oxygen transitions may be to integrate the optical density of the solvent over a range of wavelengths centered at each of the transitions. The average value of the peak width at half-height of the various solution phase emission spectra of $^1O_2(^1\Delta_g)$ available is ~35 nm. This number is probably a reflection of the slit widths used in determining the emission spectrum rather than a correct estimate of the extent of solution broadening of this transition. The area of the absorption spectra of various solvents over a 35-nm region centered at each of the transitions was used to provide a reasonable estimate of the optical density (OD) of the solvent (Table V) to test Kearn's theory.

Table V. Integrated IR Optical Densities[a] and Absorbances (in parentheses) for Various Solvents at Wavelengths That Correspond to the Three Lowest Energy Transitions of $^1O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$[b]

	integrated optical density (×10^4) (absorbance)		
solvent	4794 cm^{-1} (0–2)[d]	6314 cm^{-1} (0–1)	7874 cm^{-1} (0–0)
acetone-h_6	463 (1.24)	26.6 (0.075)	7.3 (0.0136)
acetone-d_6	18.8 (0.056)	44.2 (0.133)	0.24 (0.0004)
CH_3CN	126 (0.388)	38.4 (0.102)	6.1 (0.018)
CD_3CN	11.2 (0.027)	18.3 (0.055)	...[c]
benzene-h_6	155 (0.480)	25.0 (0.065)	3.9 (0.0084)
benzene-d_6	27.0 (0.064)	2.0 (0.008)	0.72 (0.0014)
$CHCl_3$	40.9 (0.130)	2.9 (0.007)	0.870 (0.0021)
$CDCl_3$	2.0 (0.006)	0.4 (0.0006)	...[c]
H_2O	6120 (16.4)	1350 (3.6)	166 (0.480)
D_2O	1303 (3.6)	100 (0.28)	21 (0.057)

[a] Determined by taking the area under a portion of the absorption spectrum, recorded on a Cary 14 spectrometer. See text for a more complete discussion. [b] Although some values reported in the table were determined with both 5- and 10-cm path-length solution cells, all numbers listed have been normalized to a cell path-length of 1.0 cm. [c] No absorbance could be detected, even with a 10-cm path-length cell. [d] The numbers in parentheses refer to the various oxygen transitions. In this case, $^1\Delta_g(\nu = 0) \rightarrow {}^3\Sigma_g^-(\nu = 2)$.

Table VI. Calculated Values of the Lifetime of Singlet Oxygen Using an Expression[a] of the Form Introduced by Kearns[5]

		$\tau(^1O_2)$ calcd (μs)	
solvent	$\tau(^1O_2)$ exptl value (μs)	using Kearns' coefficients[b]	using best-fit coefficients[c]
acetone-h_6	46.5 ± 2.0	60	26
acetone-d_6	690 ± 20	140	529
CH_3CN	54.4 ± 1.3	62	51
CD_3CN	600 ± 33	347	1370
benzene-h_6	26.7 ± 1.3	102	62
benzene-d_6	550 ± 11	704	347
H_2O	4[d]	2	1.5
D_2O	68.1 ± 2.5	17	9.2

[a] $k_d = a(OD)_{0-0} + b(OD)_{0-1} + c(OD)_{0-2}$. [b] $k_d(\mu s^{-1}) = 0.5(OD)_{7874\ cm^{-1}} + 0.05(OD)_{6314\ cm^{-1}} + 0.005(OD)_{4794\ cm^{-1}}$. [c] $k_d(s^{-1}) = 2.19 \times 10^7(IOD)_{7874\ cm^{-1}} + 1.07 \times 10^5(IOD)_{6314\ cm^{-1}} + 4.75 \times 10^5(IOD)_{4794\ cm^{-1}}$. IOD is the optical density integrated over a 35-nm bandwidth centered at the wavelengths shown. See text. [d] Reference 118.

Independent expressions of the form shown in eq 3 were introduced for each of the solvents investigated. The constants, *a*, *b*, *c*, etc., correspond to Franck–Condon factors in the oxygen molecule and express the extent to which a particular transition deactivates $^1O_2(^1\Delta_g)$. Using the coefficients chosen by Kearns for his set of solvents ($a = 0.5$, $b = 0.05$, and $c = 0.005$)[5] and the values for the optical density of the solvents shown in Table V, values for k_d were calculated. This exercise is a simple test of Kearns's original equation (eq 2). The results are shown in Table VI. Although a *qualitative* trend is evident, a *quantitative* correlation between calculated lifetime values and experimentally determined values is lacking. This observation has also been discussed in a preliminary report by Schuster.[41]

$$\tau(^1O_2) = a(OD)_{0-0} + b(OD)_{0-1} + c(OD)_{0-2} \qquad (3)$$

Using the experimentally determined lifetime values reported in Table I and the integrated optical densities reported in Table

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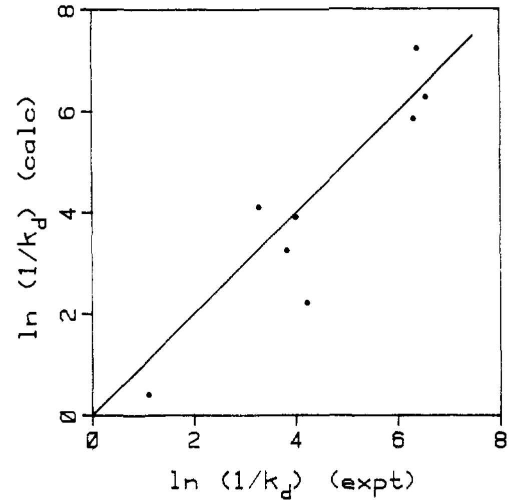

Figure 7. A plot of ln $(1/k_d)_{expt}$ vs. ln $(1/k_d)_{calcd}$ for singlet oxygen decay rate constants (k_d). k_d was calculated using eq 3. The coefficients used were $a = 2.2 \times 10^7$, $b = 1.1 \times 10^5$, and $c = 4.8 \times 10^5$. The line shown has a slope of unity.

V, empirical solutions were found for the coefficients a, b, and c in eq 3. These were then substituted back into eq 3 to yield a "calculated" value of k_d. Lifetime values determined using a set of coefficients ($a = 2.19 \times 10^7$, $b = 1.07 \times 10^5$, $c = 4.75 \times 10^5$) which provide a reasonable fit to the experimental data are also listed in Table VI. The absolute value of the coefficients reflect the units chosen for $\tau(^1O_2)$ and the optical density of the solvent (see Table VI).[100]

A plot of ln $(1/k_d)^{exptl}$ vs. ln $(1/k_d)^{calcd}$ for these constants is shown in Figure 7. Again, despite the lack of a *quantitative* correlation, it is quite evident from the data reported in Tables V and VI and Figure 7 that a *qualitative* relationship exists between the lifetime of singlet oxygen and the optical densities of the solvent. On the whole, for solvents whose optical density is large in regions that correspond to the transitions in the oxygen molecule (protiated solvents), the lifetime of singlet oxygen is short. For solvents in which near-infrared absorption is weak in the regions of interest, lifetimes tend to be longer.

For reactions in the gas phase, Ogryzlo[101,102] was also unable to find a direct correlation between quenching rate constants and the optical density of the quenching molecule for the deactivation of $^1\Sigma_g^+(O_2)$ to $^1\Delta_g(O_2)$. In his case, differences in the quenching molecules (aliphatic hydrocarbons) were not as pronounced as the differences in the solvents used in the present work. Nevertheless, a qualitative trend was also observed which suggests that, on the whole, rate constants for decay tend to increase as the optical density of the solvent increases in regions that correspond to electronic transitions in the oxygen molecule.

Since the solvent molecule must not only act as an energy sink for the energy of excitation of $^1O_2$, but must also induce the transition, and in light of the other arguments presented earlier in this section, it seems reasonable that eq 3 be rewritten in the following fashion:

$$\tau(^1O_2) \text{ or } k_d(^1O_2) = K_{solv}[a(OD)_{0-0} + b(OD)_{0-1} + c(OD)_{0-2}] \quad (4)$$

K_{solv} is a constant which is characteristic for each solvent and expresses the solvent's ability to induce a transition. K_{solv} would presumably depend on the ionization potential of the solvent (charge-transfer character in the M–O_2 complex) and the various state energy levels of the solvent. The qualitative trends noted above, however, suggest that the vibrational modes of the solvent are still quite important in the energy-transfer process. Although the various vibrational modes of the solvent are the most convenient energy sink for the energy of $^1O_2$, certain vibrational modes may also be more important than others in inducing the transition ($^3\Sigma_g^- \leftarrow {}^1\Delta_g$).[103-107] In addition, deuteration of a molecule may change the particular contribution that specific vibrational modes make to the total energy-transfer process. For instance, C–C stretching or breathing modes of a particular symmetry may not be involved in the energy-transfer process in a protiated quenching molecule. Perdeuteration of the molecule, however, may result in a situation where the C–C modes contribute in inducing the transition or in accepting energy.[103]

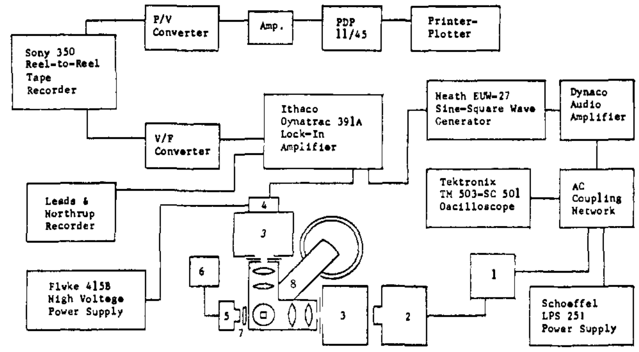

Figure 8. Block diagram of spectrofluorimeter: (1) Schoeffel lamp igniter, (2) 200-W Hg–Xe lamp in Schoeffel housing, (3) Jarrell-Ash monochromators, (4) RCA phototube in Heath housing, (5) Sylvania tungsten–halogen lamp, (6) variable-voltage transformer, (7) Corning filter, (8) Dewar pipeline (see Figure 9).

A logical extension of the arguments just presented would be an investigation of the Raman-active bands for the various solvents in the regions of the spectrum which correspond to the oxygen transitions. Both Raman- and IR-active vibrational modes together may correlate better with the observed lifetimes than IR optical densities alone, since selection rules for radiative transitions (optical densities) may not necessarily apply for nonradiative processes. Beswick and Tramer[109,110] have likewise suggested that final energy distributions cannot be accounted for simply by using Franck–Condon factors for the unperturbed molecules. These conclusions are in accord with those of Porter and others for their work on oxygen quenching of aromatic triplet states in solution.[84,108] They suggest that for the quenching process, symmetry restrictions are at least as important as Franck–Condon factors in determining the rate of energy transfer.

An attempt to correlate the lifetimes with the number of solvent vibrational quanta necessary to deactivate the 7874-cm^{-1} excitation energy of singlet oxygen may also be instructive. In this regard, protiated solvents (where values of the highest fundamental frequencies can be approximately 600 to 1000 cm^{-1} larger than those in deuterated solvents) are seen to be more efficient quenchers of singlet oxygen.[117]

The lack of an observed temperature effect on the lifetime of singlet oxygen suggests that bulk properties of the solvent are not involved in the rate-determining step of energy transfer.

In conclusion, the transition $^1O_2(^1\Delta_g) \leftrightarrow {}^3O_2(^3\Sigma_g^-)$ is an ideal model system for the study of solvent-induced energy transfer. Although Kearns' attempt to correlate transition probabilities with IR optical densities is a pioneering effort, it is an oversimplification of a very complex problem. It is indeed remarkable that a nonradiative process (the lifetime of $^1O_2$) can be characterized as well as it is by radiative processes (solvent optical densities). More

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(100) Since three parameters were used to fit the eight points in Figure 7, no quantitative significance can be ascribed to the values of the parameters.

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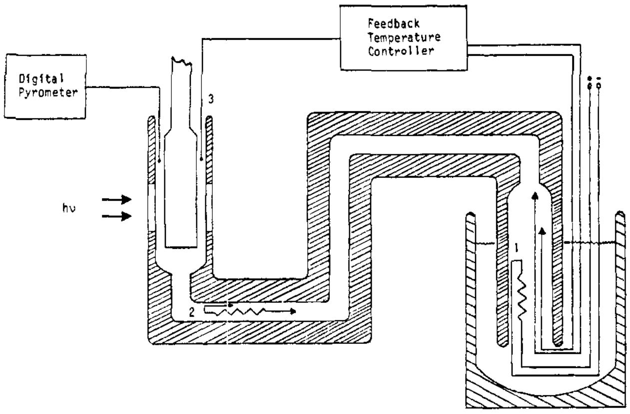

Figure 9. "Dewar pipeline": (1) boiling resistor, (2) heating resistor, (3) thermistor.

experiments which carefully vary solvent characteristics that may induce transitions will be necessary to further define the factors which govern lifetimes. These characteristics include the presence or absence of heteroatoms and π systems. Such results, together with a more complete theoretical examination, should lead to a better understanding of this important system in particular and to induced energy transfer processes in general.

III. Experimental Section

The general features of the spectrofluorimeter used in the steady-state studies have been described in detail elsewhere.[17,111,112] The entire system is shown in Figure 8, including two slight modifications not described previously. Analog voltages were conveniently stored on a magnetic tape (Sony 350 reel-to-reel tape recorder) by passing the output of the lock-in amplifier through a voltage-to-frequency converter.[113] The data could be digitized at a later time by conversion back to voltage. Steady-state low-temperature experiments were done with a "Dewar pipeline" (see below) as shown in Figure 9.

One end of the pipeline was immersed in a Dewar flask containing liquid nitrogen; a convenient flow of nitrogen gas (−196 °C) was achieved by boiling liquid nitrogen into the tube with a heating element (2000-ohm, 12-W ceramic resistor). The flowing gas was heated by a separate element (shellacked nichrome wire) connected to a feedback circuit (UCLA Chemistry Department Electronics Shop Model 3819A temperature controller). A thermistor (Victory Engineering: for temperatures greater than −115 °C, Model 21A3-1T7; for temperatures less than −115 °C, Model 05A7-2W7) suspended directly above the sample cell served as the monitoring portion of the feedback circuit. The temperature of the gas flow surrounding the cell was directly monitored with a platinum resistance thermometer connected to a digital pyrometer (Newport Labs, Inc., Model 268-PC2). The entire tube was silvered except for a window around the cell through which luminescence was excited and monitored.

A block diagram of the apparatus used in the time-resolved studies is given in Figure 10. Sensitizing dyes were excited with either the second (532 nm) or third (355 nm) harmonic of a Quanta-Ray (DCR-1) Nd:YAG laser. Laser power levels are measured by a Scientech 362 power-energy meter. A Schott KG-3 filter removed any residual fundamental radiation at 1064 nm (T at 1064 nm = 10^{-4}, T = 355 nm = 0.8, and T at 532 = 0.9). An interference filter (Oriel: 51% transmittance at 1270 nm, 5-nm width at half-height) isolated oxygen luminescence before it was focused through a Schott RG-850 cutoff filter onto an intrinsic germanium photodiode. Diodes of varying surface areas (0.25–25 mm^2, Judson Infrared, Inc.) were used with preamplifiers (UCLA Chemistry Department Electronics Shop) whose risetimes and sensitivities varied. The diode, all amplification stages, and impedance matching stages were powered by two Hewlett-Packard 6215-A power supplies maintained at ±15 V. The resultant signal was digitized by a Biomation Model 805 waveform recorder, averaged using a computer built by Drs. J. V. V. Kasper and G. Gust, and analyzed on a PDP 11/45 computer. Signals were monitored with a Tektronix 7904 oscilloscope. A Systron Donner Model 110A pulse generator provided triggering pulses for both the Biomation and the flash lamps of the laser. The emission spectrum of $^1O_2$ was recorded using an uncalibrated Bausch and Lomb grating monochromator blazed at 675 grooves/mm. Absorption spectra were recorded on a Beckman Model 25 spectrophotometer. Temperature control was achieved with the Dewar pipeline as described above.

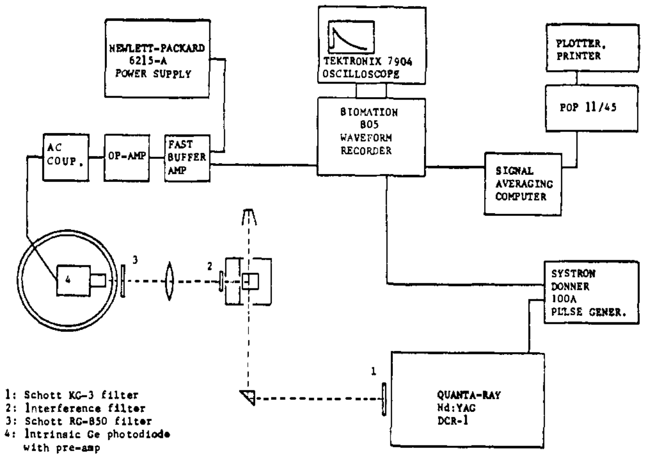

Figure 10. Block diagram of laser flash system.

Mesoporphyrin IX dimethyl ester (Sigma), zinc tetraphenylporphine (Strem), and *meso*-tetraphenylporphine (Aldrich) were used as received, 1,8-Dinaphthalenethiophene (K and K Laboratories) was recrystallized several times from toluene/ethanol/water to yield reddish-brown needles, mp 265–270 °C. Rose bengal (Eastman) was chromatographed on a 20 cm × 20 cm × 20 mm silica gel plate (E.M. Merck 60F-254 on glass) using a 20:1 (by volume) mixture of 2-butanone as eluent.[114] Product with R_f 1.6–3.9 was collected. Thionine hydrochloride (Eastman) was crystallized from a concentrated aqueous HCl solution.[115] Methylene blue chloride (Matheson Coleman and Bell) and 5,6,11,12-tetraphenylnaphthacene (rubrene) (Aldrich) were used as received. 1,3-Diphenylisobenzofuran (Aldrich) was recrystallized several times under dim lighting from benzene–ethanol to yield bright yellow needles, mp 130–131 °C. 2,3-Dimethyl-2-butene (Chemical Samples Co.) was washed with concentrated H_2SO_4 and water. After drying with Na_2SO_4, the liquid was refluxed over sodium and then distilled.[116] 1,4-Diazabicyclo[2.2.2]octane (Dabco) (Aldrich) was recrystallized three times from acetone and stored under nitrogen unit used.[115]

Mallinckrodt protiated spectrograde solvents were used; 99.5 atom % D acetone (Aldrich), 99.0 atom % D acetonitrile (Aldrich), 99.8 atom % D chloroform (Merck, Sharpe, and Dohme), 99.5 atom % D benzene (Alfa and Aldrich), and 99.8 atom % D D_2O (Stohler) were used.

For the protiated solvents, no effect was observed when the solvent was stored over molecular sieves. A slight decrease (~20%) in the lifetime of singlet oxygen occurred when the deuterated solvents were so stored. For most of the experiments, solutions were air saturated. No difference was seen in the lifetime upon oxygen saturation of the solutions.

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Registry No. O_2, 7782-44-7; D_2, 7782-39-0; acetone, 67-64-1; acetonitrile, 75-05-8; benzene, 71-43-2; trichloromethane, 67-66-3.

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