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SOLVENT AND DEUTERIUM ISOTOPE EFFECTS ON THE LIFETIME OF SINGLET OXYGEN DETERMINED BY DIRECT EMISSION SPECTROSCOPY AT 1.27 µm

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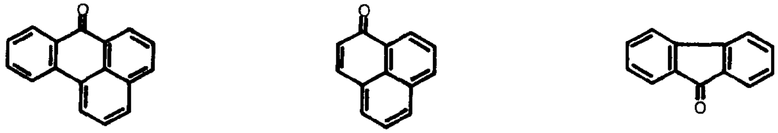
ABSTRACT. The relative lifetimes of singlet molecular oxygen have been evaluated, as a function of solvent and deuterium substitution, via measurement involving the direct emission of singlet oxygen at 1.27 µm.

INTRODUCTION. An accurate value of the lifetime of singlet molecular oxygen ($^1\Delta_g$) in solution is of paramount importance in the evaluation of the rate constants for reaction of this important reactive intermediate. Although data in the literature show general agreement for the lifetime of singlet molecular oxygen in solvents for which the inherent lifetime appears to be less than about 100 µs,[1] there is considerable disagreement[2,3] with respect to the reported values of the lifetime of singlet oxygen in solvents such as CCl_4, $CDCl_3$, $C_6D_5CD_3$. For example, indirect chemical methods for lifetime determination have generally led to shorter lifetimes than methods based on direct analysis of the decay of the emission of singlet oxygen at 1.27 µm. Recently, Foote[4] reported rather large effects on solvent deuteration which imply longer lifetimes than previously reported in solvents such as $CDCl_3$, C_6D_6, CD_3CN, and $(CD_3)_2CO$. Lifetimes approaching tens of ms have now been reported in certain solvents. The calculated radiative lifetime of singlet oxygen in the vapor phase[5] implies an unreasonably low quantum yield ($<10^{-6}$) for emission from singlet oxygen in solution. However, the recently estimated value of 4 s in CCl_4 [6] based on an absolute quantum yield of 4×10^{-3} removes this dilemma. Evidently, solvent collisions induce a much shorter inherent radiative lifetime for singlet oxygen in solution. However no significant variation of the radiative lifetime in different solvents has been found.[6]

We report here an investigation of the emission of singlet oxygen (1.27 µm) in a variety of organic solvents with the intention of determining by a direct spectroscopic method the relative lifetimes of singlet oxygen in these solvents. The basis of the method is to start with a solvent in which the lifetime of singlet oxygen is very long and then to determine the singlet oxygen lifetimes as a function of added cosolvent.

RESULTS AND DISCUSSION. The steady state method[7] used in this work yields relative lifetimes of singlet oxygen. Typically, a 10^{-5} M stirred solution of a sensitizer (7H-benz[de]anthracen-7-one, phenalenone or fluorenone, Scheme I) in CCl_4 was irradiated at 366 nm and the steady state


7H-Benz[de]anthracen-7-one (1) Phenalenone (2) Fluorenone (3)

Scheme I Sensitizers Employed in this Study emission (I_o) at 1.27 µm was recorded Addition of portions (x, in fractions of the total volume) of a different solvent caused an emission signal decrease It was found that after correction for O.D. changes, the Stern-Volmer kinetic law (Eqn. 1) was followed over the range investigated (up to 20% mixtures, typical plot shown in Figure 1).

$$I_o/I = \beta x + 1 \qquad \text{where } \beta = \tau_{CCl_4}/\tau_{solvent} \qquad (1)$$

The behavior of singlet oxygen in benzene was employed as a standard because in this solvent, the values reported for singlet oxygen lifetimes in the literature[8] differ only within the error limits (25 ± 3 µs) Eqn. 2 was employed to determine the values given in Table 1.

$$\tau = \tau_{C_6H_6} \left(\beta_{C_6H_6}/\beta_{solvent}\right) \qquad (2)$$

For investigation of solvents in which singlet oxygen exhibits long lifetimes (> 1 ms), a modified method was used, e.g., a small portion of a concentrated solution of the sensitizer in CCl_4, typically 10 µl, was diluted by 2.0 ml of a neat solvent and the corresponding emission signals were recorded. The results presented in Table 2 are relative quantum yields, and refer to the emission intensity obtained from a CCl_4 solution which was checked frequently in order to establish that fluctuations in the exciting light intensity, temperature of the probe and detector response were below the actual accuracy of the emission intensity determination.

The choice of the sensitizers used in this investigation was dictated by the experimental conditions of this work, which require high singlet oxygen concentrations [9] In the absence of quencher, numerous "well established" sensitizers for singlet oxygen generation such as Rose Bengal, Methylene Blue, and anthracene, for example, rapidly react, whereas benzophenone and benzophenone derivatives (although stable under the above conditions) produce a considerably lower emission signals compared to the sensitizers used in this investigation.

As the lifetime of a reactive intermediate such as singlet oxygen gets longer and longer, the measured experimental lifetime becomes critically dependent on the precise experimental conditions. For example, minor "impurities", which play no significant role in determining the lifetime when solvent deactivation is fast, can become lifetime controlling Thus, the ground state of the sensitizer used to produce singlet oxygen, long-lived excited states or products derived from photoexcitation of the sensitizer, ground state triplet oxygen and singlet oxygen itself may become "impurities" that determine the measured lifetime. In spite of these technical problems, we believe that our method validly measures solvent properties rather than impurity properties because no change of the emission signal with time is observed;[10] secondly, the lifetimes obtained in this work are considerably longer than previously reported;[1-4] and furthermore, the light intensity employed[13] yielded, at the low sensitizer concentrations used in this study (∿ 10^{-5}M), steady state singlet oxygen concentrations which have been established by time resolved measurements[14] to lie well below the limit at which singlet oxygen is deactivated by bimolecular mechanisms.

Several theories have been presented to rationalize the different lifetimes of singlet oxygen in various solvents.[8c,11,15b] Quenching of singlet oxygen by organic solvents is much less efficient than the specific quenching by chemical or physical quenchers (Table 1)

Table 1. Lifetimes and Deuterium Effects of Singlet Oxygen in Organic Solvents.

Solvent[a]	Lifetime τ (μs) H	Lifetime τ (μs) D	k_q in CCl_4 ($M^{-1}s^{-1}$) H	k_q in CCl_4 ($M^{-1}s^{-1}$) D	τ_D/τ_H	Lit. (D/H)
Chloroform	160 ± 6	3600 ± 150	500 ± 20	22 ± 1	22.5 ± 1	10 ± 1 [4]
Methylenechloride	59 ± 6	120 ± 10	1100 ± 100	530 ± 40	2.0 ± .5	----
Acetone	39 ± 1	770 ± 100	1880 ± 50	95 ± 12	19.7 ± 3	18 ± 2 [4]
Acetonitrile	58 ± 3	950 ± 70	900 ± 50	55 ± 4	16.4 ± 2	8 ± 1 [4]
Benzene	25[b]	680 ± 30	3600 ± 300	131 ± 6	27.2 ± 1	16 ± 1 [4]
Toluene	27 ± 2	310 ± 20	3900 ± 300	340 ± 20	11.5 ± 1	11 ± 1.5 [3]
Cyclohexane	17 ± 2	320 ± 30	6350 ± 800	340 ± 30	18.1 ± 3	----

(a) Air saturated at 25°C, (b) Literature[8] value, taken as reference.

Table 2. Lifetimes of Singlet Oxygen in Halogenated Organic Solvents.

Solvent[a]	Φ_{CCl_4}/Φ	τ (ms)	Lit. (ms)
CCl_4	1	31 ± 2[b]	26 ± 1 [2]
CCl_2FCClF_2	74 ± 1	42 ± 4	2.3 [1]
C_6F_6	3.3 ± .2	9.4 ± .3	.59 [1]
$(C_2F_5)_2O$	28 ± 3	1.1 ± .1	---

(a) Air saturated at 25°C; (b) Referred to lifetime in benzene.

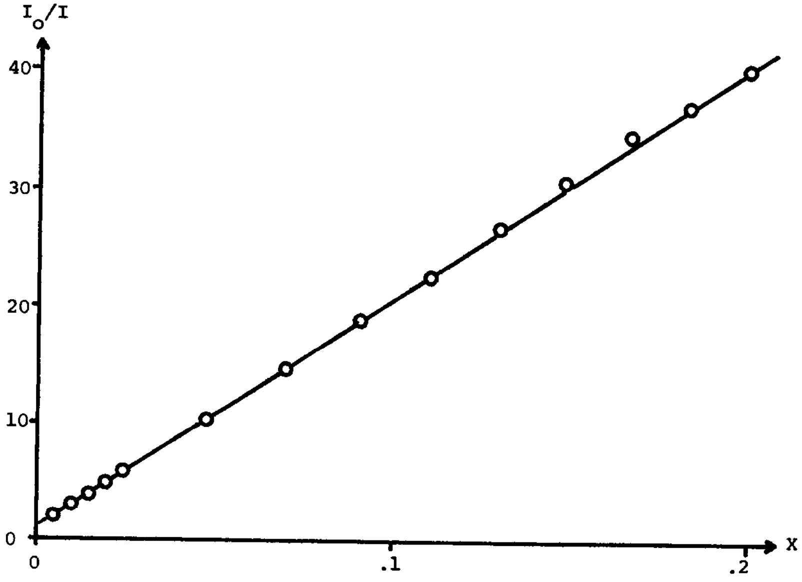


Figure 1. Singlet Oxygen Emission (1.27 μm) in CCl_4 Quenched by $CHCl_3$.

Although this partial correlation[11,15a] is intriguing and somewhat puzzling, it suggests that an electronic to vibronic coupled transition is involved in the quenching mechanism of singlet oxygen for rate constants $k_q < 10^4\ S^{-1}$.

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9. Steady-state concentrations of singlet oxygen as high as 10^{-5} M could be readily achieved in CCl_4. The response of the detector system was calibrated with the emission from singlet oxygen formed during thermal decomposition of 1,4-dihydro-1,4-dimethylnaphthalene-1,4-endoperoxide in CCl_4, using the known yield of singlet oxygen and the decomposition rate. (See ref. 12 below)
10. In solvents in which singlet oxygen exhibits a long lifetime (>10 ms) even 1,4-diazobicyclo-[2.2 2]octan (DABCO), a widely used physical quencher for singlet oxygen, reacts irreversibly.
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14. Time resolved emission measurements following laser excitation of the same sensitizers (1 to 3) at 355 nm in all solvents with τ > 500 μs confirmed the reported lifetimes For example, the lifetime of $^1O_2$ in $CDCl_3$ extrapolated to zero laser intensity is 3600 ± 300 μs The number from the steady state method is 3600 ± 150 (Table 1) Furthermore, our values are in good agreement with the lifetimes recently reported and measured by a time-resolved methods. (See reference 15 below) However, a laser power dependence of the lifetimes was found as well as second order contributions at laser powers > 1 mJ
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