that the trans–cis dicinnamate, TC, is inert with respect to the cycloaddition reaction, but the computation of the apparent quantum efficiency Φ_{cy} involves photons absorbed by trans species in both TT and TC compounds. The extrapolated quantum efficiency, where the ratio of cis/trans = 0, requires no correction since only TT is present.

The reason for the variation in the apparent quantum efficiency of the trans → cis isomerization is due to the well-known photoreversibility of this reaction.[1] The main objective of this study was to obtain relative efficiencies of the cycloaddition and the isomerization reactions. The values for the apparent quantum efficiencies of the latter as a function of cis/trans ratios are given in Table II and represented in Figure 3. The efficiency of the trans → cis isomerization is the $\Phi_{trans \rightarrow cis}$ intercept, and its value is 0.473. The extrapolated value obtained for the photocyclization is 0.086. The ratio of the efficiencies, $\Phi_{cy}/\Phi_{trans \rightarrow cis}$ is remarkably high. This is ascribed to and consistent with the concept that pairs of cinnamoyl groups have been forced into close proximity, a situation analogous to that of the solid state. The efficiency of the photocyclization reaction is approximately 18% of the value of the photoisomerization reaction. For synthetic purposes, one should be able to obtain nearly theoretical yields of cyclobutane products since the trans–trans compound is irreversibly removed from the reaction mixture, and the equilibrium is shifted toward more trans–trans formation.

Radiationless Decay of Singlet Molecular Oxygen in Solution. An Experimental and Theoretical Study of Electronic-to-Vibrational Energy Transfer

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Abstract: A Q-switched ruby laser has been used to spectroscopically measure the lifetime of singlet ($^1\Delta$) oxygen in solution. The nature of the solvent is found to have a remarkable effect on the lifetime of singlet oxygen with values ranging from 2 μsec in water to 700 μsec in CCl_4. A simple theory has been developed to account for the quenching of $^1\Delta$ by the solvent in terms of intermolecular electronic-to-vibrational energy transfer. According to this theory the quenching efficiency can be quantitatively related to the intensities of infrared overtone and combinational absorption bands of the solvent in the energy regions of $^1\Delta \rightarrow {}^3\Sigma$ transitions and especially near 7880 and 6280 cm^{-1}, the respective 0 → 0 and 0 → 1 oxygen transition energies. Direct calculation of the quenching rates using this theory with no adjustable parameters yields a better than order of magnitude agreement with experimental results. An analysis of gas phase and solution quenching rate constants indicates rate constants obtained in one phase may be used to compute quenching constants in the other phase. This applies to the quenching of $^1\Sigma$ as well as $^1\Delta$. The apparent lack of a heavy atom effect on the $^1\Delta$ lifetime can be accounted for. Large deuterium effects are predicted and observed. The theory indicates that the quenching involves a second-order indirect mixing of $^3\Sigma$ and $^1\Delta$ states through $^1\Sigma$ by interaction with the solvent, in which $^3\Sigma$ and $^1\Sigma$ are mixed *via* an intramolecular spin–orbit coupling. Mixing of $^1\Sigma$ and $^1\Delta$ is also important in the quenching of $^1\Sigma$, and the matrix elements used to account for the observed quenching rate constants for $^1\Delta$ automatically lead to rate constants for the quenching of $^1\Sigma$ which are in good agreement with the experimental values. The theory thus appears to be internally consistent. The techniques used to measure the solvent-controlled decay of singlet oxygen have also been used to evaluate the absolute rate constants for the reaction of singlet oxygen with various acceptors. A quantum yield of 0.9 ± 0.1 was measured for the formation of $^1\Delta$ from quenching of triplet state methylene blue. The quenching of singlet oxygen by β-carotene and a polymethene pyrylium dye (I) has been investigated. We confirm the earlier suggestion by Foote that the β-carotene quenching of singlet oxygen is nearly diffusion controlled ($2 \times 10^{10}\ M^{-1}\ sec^{-1}$ in benzene). The rate constant for the quenching of $^1\Delta$ by I is found to be $3 \times 10^{10}\ M^{-1}\ sec^{-1}$ in acetonitrile. The discrepancy between our observation that the lifetime of $^1\Delta$ is extremely solvent sensitive and earlier indications that the lifetime is relatively solvent independent is resolved. Our findings indicate the factors which may permit $^1\Delta$ lifetimes of greater than 1 msec in appropriate solvents to be obtained.

Recognition of the importance of singlet molecular oxygen as an intermediate in the photooxidation of unsaturated hydrocarbons has stimulated much of the current interest in the chemical and physical properties of this species.[1–4] One of the most common methods of generating singlet oxygen is *via* energy transfer from an excited triplet sensitizer to ground-state oxygen. With sensitizers having a lowest triplet state above 13,100 cm^{-1}, both $^1\Sigma$ and $^1\Delta$ oxygen are produced.[5–9] However, for solution-phase reactions

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(1) C. S. Foote and S. Wexler, *J. Amer. Chem. Soc.*, **86**, 3879 (1964).

(2) E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3881 (1964).

(3) K. Gollnick, *Advan. Chem. Ser.*, No. 77, 78 (1968).

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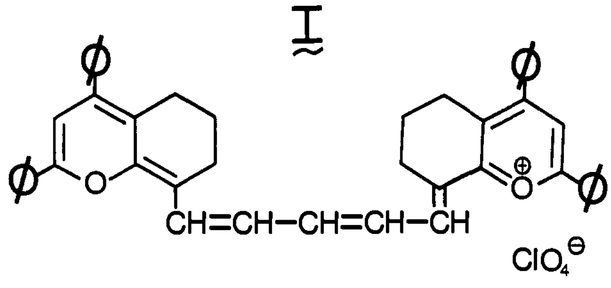

Figure 1. Polymethene pyrylium dye (I).

only ${}^1\Delta$ is expected to be important due to the short lifetime ($\lesssim 10^{-10}$ sec) estimated[10] for ${}^1\Sigma$.

Under usual photooxygenation conditions the two important competitive decay modes for ${}^1\Delta$ are physical quenching to the ground ${}^3\Sigma$ state

$$ {}^1\Delta \xrightarrow{1/\tau} {}^3\Sigma \qquad (1)$$

and chemical reaction of ${}^1\Delta$ with an acceptor A

$$ {}^1\Delta + \mathrm{A} \xrightarrow{k_a} \mathrm{AO_2} \qquad (2)$$

where AO_2 denotes the peroxide products. Steady-state measurements of photooxidation quantum yields as a function of concentration have allowed the determination of $\beta = (1/\tau k_a)$.[4] Physically, β represents the concentration of acceptor required to intercept half of the singlet oxygen produced, and thus it serves as an index of relative acceptor reactivities, but it does not permit either the absolute value of the reaction rate constant or the ${}^1\Delta$ lifetime to be determined unless one is known from other experiments.

We have recently reported a direct measurement of the lifetime of singlet oxygen and of absolute acceptor rate constants in methanol[11] as well as in other solvents.[12]

In this paper we have carried out a more comprehensive experimental and theoretical study of solvent effects on the lifetime of ${}^1\Delta$. We find that there are pronounced solvent effects on the decay of singlet oxygen, with lifetimes varying over almost three orders of magnitude. A strong correlation is noted between the singlet oxygen lifetime and the infrared absorption intensity of the solvent overtone and combinational bands in near resonance with the ${}^1\Delta \rightarrow {}^3\Sigma$ transition frequencies. Our experimental observations and theoretical considerations lead us to propose that the major pathway for radiationless decay of the ${}^1\Delta$ state involves conversion of electronic energy of oxygen directly into vibrational excitation of the solvent. The behavior of oxygen, a prototype small molecule in which the rate of intramolecular electronic relaxation is very slow, is to be contrasted with the behavior of large molecules where intramolecular relaxation of electronically excited states is rapid.

Experimental Section

Materials. With the exception of distilled water, deuterium oxide (Mallinckrodt 99.8%), perdeuterioacetone (Stohler Isotope Chemicals 99.5%), and absolute ethanol, solvents were Matheson Coleman and Bell Spectroquality. Methylene blue (MB) was obtained also from Matheson Coleman and Bell. Aldrich 1,3-diphenylisobenzofuran (DPBF) was purified by recrystallization from methanol-water. Rubrene, also from Aldrich, was used without further purification. Fresh samples of 2,5-dimethylfuran (99%), 2,4-dimethylbutene (99%), 1,3-dimethylcyclohexene (98%), and 2,5-dimethyl-2,4-hexadiene (99%) from Chemical Samples Co. were used as received. Sigma Chemical β-carotene was purified by recrystallization from a mixed benzene-methanol solvent. The polymethene pyrylium dye (I) shown in Figure 1 was a gift from J. Williams of Eastman Kodak.

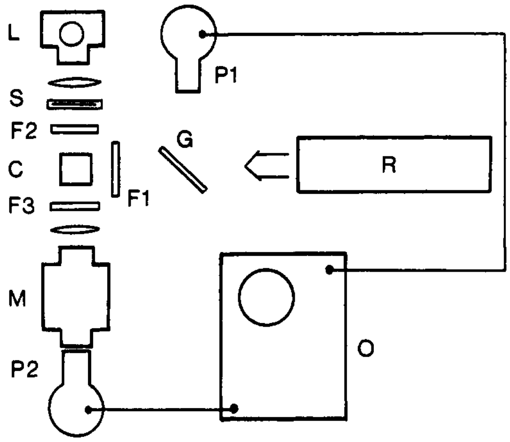

Figure 2. Schematic of laser photolysis apparatus: R (ruby laser), P1 (triggering photomultiplier), L (analyzing lamp), M (monochromator), P2 (monitoring photomultiplier), C (sample cell), S (shutter), G (glass plate), F1 (Corning 2-64 filter), F2 (5-60 filter), F3 (4-96 filter), O (oscilloscope).

Methods. A ruby laser pulse was used to excite the sensitizer methylene blue (10^{-5}–10^{-4} M) in oxygenated or air-saturated solutions. With the 1-J laser pulse, conversion to triplets is essentially complete. The monomer and dimer triplets are quenched by ground-state oxygen in <0.5 μsec forming singlet oxygen with an efficiency near unity.[13] As a probe of the singlet oxygen concentration the acceptor 1,3-diphenylisobenzofuran ($\beta \sim 10^{-4}$)[14,15] was added to the solution, and the rate of decrease in absorption (λ_{max} ~410 nm) as a result of peroxide formation following a laser pulse was monitored.

The combination of MB and DPBF is well suited for these laser kinetic experiments since MB exhibits strong absorption at the fundamental ruby wavelength, while the absorption of DPBF occurs in a region in which MB is nearly transparent. An acceptor with a very low β value is required since the maximum fractional bleaching can be shown to equal $[{}^1\Delta]_0/\beta$, $[{}^1\Delta]_0$ being the concentration of singlet oxygen produced by the light pulse. Furthermore, in the investigation of the effect of addition of another acceptor on the decay of singlet oxygen, it is desirable that the concentration of the acceptor remain nearly constant during the bleaching of DPBF. This condition requires that β for DPBF be substantially smaller than that of the second acceptor.

A schematic diagram of the experimental apparatus is given in Figure 2. A Q-switched (cryptocyanine passive dye cell) ruby laser, constructed in this laboratory, was used to deliver 694-nm pulses of ~20-nsec duration. Transient absorption produced in a 1-cm square cell was monitored at 90° to the exciting laser beam. The analyzing unit consisted of a 650-W tungsten-iodine lamp, a Bausch and Lomb high intensity monochromator, an RCA 1P28 photomultiplier (P2), and a Tektronix 545A monitoring oscilloscope, equipped with a Type 1A1 plug-in unit. The oscilloscope was triggered synchronously with the laser pulse by a second photomultiplier (P1) which viewed a portion of the laser light.

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(10) S. J. Arnold, M. Kubo, and E. A. Ogryzlo, *Advan. Chem. Ser.*, No. 77, 133 (1968).

(11) P. M. Merkel and D. R. Kearns, *Chem. Phys. Lett.*, 12, 120 (1971).

(12) P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, 94, 1029 (1972).

(13) Second-order rate constants for oxygen quenching of dimer and monomer triplets are of the order of 3×10^9 M^{-1} sec^{-1} (*e.g.*, 2×10^9 M^{-1} sec^{-1} for monomer quenching in methanol), and lifetimes of monomer and dimer triplets in deoxygenated solution while solvent and concentration dependent are in the neighborhood of 10 μsec (*e.g.*, 7 μsec for monomer in a 10^{-4} M solution of MB in methanol).

(14) I. B. C. Matheson and J. Lee, *Chem. Phys. Lett.*, 7, 475 (1970).

(15) R. H. Young, K. Wherly, and R. Martin, *J. Amer. Chem. Soc.*, 93, 5774 (1971).

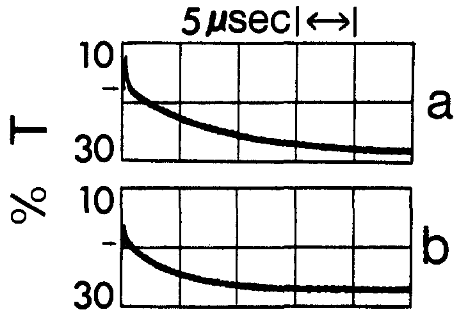

Figure 3. Bleaching in an oxygenated solution of methylene blue (10^{-4} M) in methanol of (a) 1.5 × 10^{-5} M 1,3-diphenylisobenzofuran monitored at 410 nm in a 1-cm cell and (b) 1.0 × 10^{-4} M 1,3-diphenylisobenzofuran monitored at 435 nm in a 2-mm cell. Arrows indicate % T before the pulse.

Under normal circumstances the signal-to-noise ratio in the photoelectric measurement of transient absorption is limited by the photocathode current. The maximum value of the photocathode current is in turn fixed by the gain of the photomultiplier and the space charge limited anode current. Reduction of the photomultiplier gain allows an increase in photocathode current without overloading the anode. This was accomplished by using only the first seven dynodes of the 1P28, the last of which constituted the collector. Dynodes 8 and 9 and the anode were connected to ground through a resistor. A tenfold increase in the signal-to-noise ratio was obtained with this arrangement.

Excitation of MB by the analyzing light can itself produce significant bleaching of DPBF. This problem was virtually eliminated by positioning a shutter, which was manually opened immediately prior to triggering the laser, and a Corning 5-60 band pass filter between the lamp and sample cell.

Steady-state measurements of methylene blue sensitized photobleaching of rubrene were carried out in acetone and perdeuterioacetone in a manner reported previously.[16]

Results

1. Measurement of $^1\Delta$ Lifetime and Solvent Effects. Under conditions where [A] does not change substantially during the course of an experiment, solution of the kinetic equations describing processes 1 and 2 yields

$$[AO_2] - [AO_2]_\infty = \frac{k_a[A][^1\Delta]_0}{(1/\tau) + k_a[A]} e^{-(1/\tau + k_a[A])t} \qquad (3)$$

where $[AO_2]_\infty$ is the concentration of peroxide after all singlet oxygen produced in a pulse has decayed. From this it follows that

$$-2.3 \log ([A] - [A]_\infty) = ((1/\tau) + k_a[A])t + \text{constant}$$

which can more conveniently be expressed as

$$-2.3 \log (OD - OD_\infty) = ((1/\tau) + k_a[A])t + \text{constant}$$

where OD is the optical density of the acceptor at time t and OD_∞ is the asymptotic value. Plots of ($OD - OD_\infty$) *vs.* t for two acceptor concentrations yield values for both τ and k_a.

Laser-induced photobleaching of DPBF is illustrated in Figure 3. In Figure 3a an acceptor concentration of 1.5 × 10^{-5} M results in a decay rate fixed primarily by τ. The initial short-lived transient absorption arises from MB triplet–triplet absorption. In a deoxygenated solution no bleaching is observed and the MB triplet decays at the same rate as observed in the absence of DPBF, thus eliminating the possibility of direct reaction between acceptor and sensitizer. Increasing the acceptor concentration to 10^{-4} M noticeably decreases the duration of photobleaching by consumption of a significant portion of $^1\Delta$ as is demonstrated in Figure 3b.

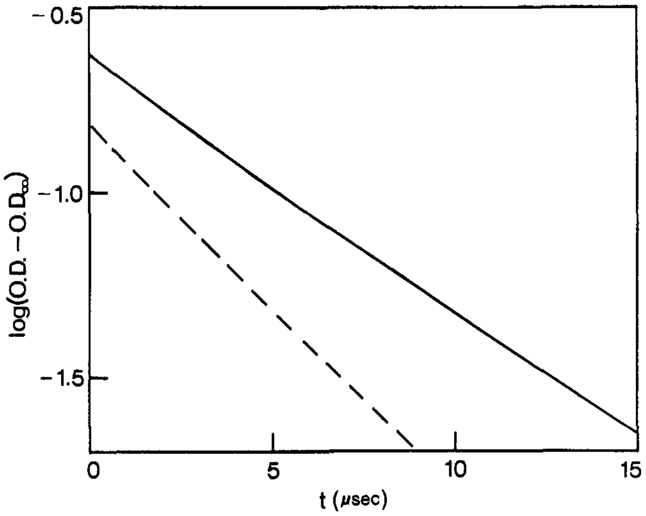

Figure 4. First-order decay plots of (a) —— and (b) - - - - - of Figure 3.

First-order plots of the decay curves in Figures 3a and 3b appear in Figure 4. The slight curvature reflects the consumption of acceptor as photooxidation progresses. From the slopes of these two plots we calculate $\tau(CH_3OH)$ = 7 μsec and k_a(DPBF) = 8 × 10^8 M^{-1} sec^{-1}.

The same procedures were used to measure the $^1\Delta$ lifetimes in ten additional solvents. Concentrations of methylene blue were chosen in each case such that fractional bleaching was small enough to prevent substantial departures from first-order linearity.

To solubilize the methylene blue, 1% methanol was added to the carbon disulfide and carbon tetrachloride solutions, while cyclohexane and benzene contained 2% methanol. The decay component due to the methanol was extracted from the observed decay by subtracting the appropriate fraction of the decay constant ($1/\tau$) for pure methanol. Although this procedure may only be approximately correct, the correction factor is relatively large only in the case of carbon tetrachloride.

The lifetime for water was extrapolated from the data for pure methanol and 50% methanol–50% water. This procedure was necessitated by the insolubility of DPBF in water and by the marked decrease in the reaction rate constant for DPBF in solutions containing more than ~70% water. The latter phenomenon probably arises from dimerization of the DPBF (the absorption spectrum red shifts and fluorescence disappears).

Bleaching of DPBF in 50% water–50% methanol and in carbon disulfide is shown in Figures 5a and 5b, respectively. These two decay curves illustrate the strong dependence of the lifetime of singlet oxygen upon solvent. The decay measurements are summarized in Table I. Lifetimes range from 2 μsec in water to approximately 700 μsec in carbon tetrachloride. They are estimated to be accurate to within 20% except for CS_2 (~30%) and CCl_4 (~50%). Solvent optical densities (1-cm cell) at 7880 and 6280 cm^{-1} are

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[16] P. B. Merkel, R. Nilsson, and D. R. Kearns, *J. Amer. Chem. Soc.*, 94, 1029 (1972).

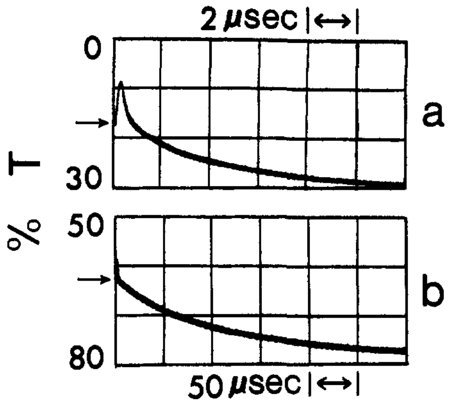

Figure 5. The decay of $^1\Delta$ as monitored by DPBF in (a) oxygenated 50% H_2O-50% CH_3OH with 1.5×10^{-5} M DPBF and 5×10^{-5} M MB (at 410 nm), and in (b) air-saturated CS_2 (containing 1% CH_3OH) with 0.5×10^{-5} M DPBF and 2×10^{-5} M MB (at 415 nm). Note the different time scales for (a) and (b).

Table I. Lifetimes of Singlet Oxygen in Various Solvents

Solvent	$\tau^1\Delta$, μsec	$OD_{7880\ cm^{-1}}$ (1 cm)	$OD_{6280\ cm^{-1}}$ (1 cm)
H_2O	2[a]	0.47	3.4
CH_3OH	7	0.18	3.9
50% D_2O-50% CH_3OH	11	0.09	1.0
C_2H_5OH	12	0.14	2.0
C_6H_{12}	17	0.09	0.08
C_6H_6	24	0.009	0.11
CH_3COCH_3	26	0.015	0.08
CH_3CN	30	0.016	0.14
$CHCl_3$	60	0.002	0.01
CS_2	200	<0.0005	0.00
CCl_4	700	<0.0005	0.00

[a] Extrapolated from data obtained using 1:1 mixture of H_2O and CH_3OH.

also listed in Table I. The significance of these quantities will be explained in the Discussion and in the Theoretical Section.

Lifetimes measured in oxygen saturated ($\sim 10^{-2}$ M) solutions were not noticeably different from those obtained in air-saturated solutions. This sets an upper limit of 10^6 M^{-1} sec^{-1} for the bimolecular rate constant for the quenching of $^1\Delta$ by $^3\Sigma$ oxygen in solution. In some cases slight increases in photooxidation yields were observed with oxygen bubbling due to the more effective competition of oxygen quenching of dye triplets with other nonradiative decay processes (unimolecular decay, triplet-triplet annihilation, dimer quenching of monomer triplets, and quenching of singlet oxygen itself by triplet-state sensitizer).[17]

Mutual annihilation of two $^1\Delta$ molecules provides another possible decay channel.[10] The absence of a second-order component in the singlet oxygen decay curves and lack of effects arising from changes in $[^1\Delta]_0$ (achieved by varying the dye concentration) indicate that the annihilation rate constant in solution is $< 10^9$ M^{-1} sec^{-1}.

2. Deuterium Effects on the Lifetime of Singlet Oxygen. The observation that there are large solvent effects on the lifetime of singlet oxygen[12] suggested that it would be worthwhile to investigate further the effect of deuteration of the solvent on τ. Comparison of photooxidation efficiencies in nondeuterated and deuterated solvents under a fixed set of conditions has been used to obtain $^1\Delta$ lifetimes in the latter.[16] In the present studies the efficiency of rubrene photooxidation was observed to be the same (within an experimental accuracy of ±20%) in acetone and perdeuterioacetone. This indicates a singlet oxygen lifetime in perdeuterioacetone of approximately 26 μsec. These results along with those reported previously[16] are summarized in Table II. An interpretation of the deuterium effects will be presented later, and the optical densities which are listed in Table II are important in this respect.

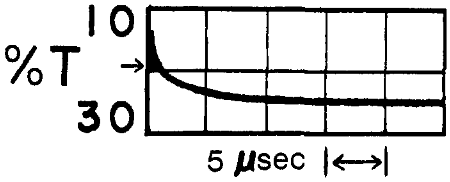

Figure 6. Same conditions as Figure 3a but with 5×10^{-3} M 2,4-dimethyl-2-butene added.

Table II. Deuterium Effects on the Lifetime of Singlet Oxygen

Solvent	$\tau^1\Delta$, μsec	$OD_{7880\ cm^{-1}}$ (1 cm)	$OD_{6280\ cm^{-1}}$ (1 cm)
H_2O	2	0.47	3.4
D_2O	20	0.06	0.27
H_2O:CH_3OH, 1:1	3.5	0.33	3.7
D_2O:CH_3OH, 1:1	11	0.10	1.0
D_2O:CD_3OD, 1:1	35	0.03	0.30
CH_3COCH_3	26	0.015	0.08
CD_3COCD_3	26	0.002	0.13

3. Quantum Yield for Formation of $^1\Delta$ from Triplet Sensitizer. In dilute oxygenated solutions where only monomer dye is present, oxygen quenching is the only important decay mode for ^{3}MB. If the [DPBF] is kept low enough so as not to influence the decay of $^1\Delta$, then $[^1\Delta]_0 = \beta[AO_2]_\infty/[A]$. Comparison of $[^1\Delta]_0$ and the initial [^{3}MB] under such circumstances has allowed us to determine that $^1\Delta$ is formed (either directly or from $^1\Sigma$) with an efficiency of 0.9 ± 0.1 when methylene blue triplets are quenched by oxygen. This result is in agreement with the theoretical prediction that for a molecule like MB oxygen quenching by energy transfer will predominate over quenching by enhancement of intersystem crossing to the ground state.[5]

4. Absolute Reaction Rate Constants. The disappearance of DPBF in a solution containing a second chemical or physical quencher of singlet oxygen, Q, having a quenching constant k_Q can be expressed in terms of

$$\log(OD - OD_\infty) = -2.3^{-1}((1/\tau) + k_A[A] + k_Q[Q])t + \text{constant}$$

Since τ and k_a(DPBF) have been measured as described previously, k_Q can be calculated from a first-order decay plot for a given [DPBF] and [Q].

If Q is an acceptor which quenches solely by reacting with singlet oxygen, then k_Q is the reaction rate constant k_a. The effect of 5×10^{-4} M 2,4-dimethyl-2-

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(17) C. K. Duncan and D. R. Kearns, *Chem. Phys. Lett.*, **10**, 306 (1971).

butene on the decay of singlet oxygen is depicted in Figure 6. Both the duration and yield of DPBF photooxidation are decreased (compare with Figure 3a). An acceptor rate constant of k_a(2,4-dimethyl-2-butene) = $4 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ is calculated from the first-order plot of this bleaching curve. Absolute rate constants in methanol obtained in this manner for a series of common acceptors are given in Table III. Probable error limits are ±25%. Where comparison is possible, the resulting β values are in reasonable agreement with those obtained in methanol by steady-state methods.[15,18] It should be noted that as in the steady-state methods the presence of a small component in rate constant due to purely physical quenching cannot positively be ruled out.

Table III. Absolute Acceptor Reaction Rate Constants in Methanol

Acceptor	k_a, M^{-1} sec^{-1}
1,3-Diphenylisobenzofuran	8×10^8
2,5-Dimethylfuran	4×10^8
2,4-Dimethyl-2-butene	4×10^7
1,2-Dimethylcyclohexene	1×10^7
2,5-Dimethyl-2,4-hexadiene	2×10^6

Reaction rate constants for DPBF were not observed to be highly solvent dependent, varying only by about a factor of 2 over the range of solvents studied (excepting water).

5. **Quenching of $^1\Delta$ by β-Carotene and I.** Some time ago Foote and coworkers found β-carotene to be an extremely effective inhibitor of singlet oxygen reactions.[19,20] By assuming that β-carotene physically quenches singlet oxygen at a diffusion-controlled rate, they have been able to estimate a lifetime for $^1\Delta$ of 10^{-5} sec in a 4:1 benzene-methanol solution.[20] We have now been able to directly measure the β-carotene quenching of $^1\Delta$ and find $k_Q = 2 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ in benzene. The polymethene pyrylium dye (I) is found to be a similarly efficient quencher of $^1\Delta$. In acetonitrile a value of $k_Q = 3 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ is obtained for this dye.

Discussion

1. **Solvents Effects on $^1\Delta$ Lifetime.** Prior to the present work the lifetime of singlet oxygen was commonly believed to be nearly independent of solvent. This view was based on observations that β values for some common acceptors were not strongly dependent upon the nature of the solvent.[4,21,22] In contrast, large solvent effects (of the same order as our directly measured lifetimes would indicate) were observed on the rate of photooxidation of anthracene.[23] These results have recently been confirmed by Foote.[24] The results of our measurements, presented in Table I, demonstrate that there are very large solvent effects on the $^1\Delta$ lifetime. The apparent discrepancy between our work and the earlier studies may be traced in part to the use of mixed solvent systems and to solvent effects on reaction rate constants which tend to obscure lifetime variations in the steady-state experiments. Furthermore, the extremes in our measurements, water and carbon tetrachloride, have not previously been studied.

Examination of the data presented in Table I clearly indicates that the $^1\Delta$ lifetime is uncorrelated with most of the usual solvent properties. Contrary to the suggestion of Young and coworkers[25] no correlation between the lifetime of singlet oxygen and solvent polarity is indicated. For example, the lifetime of $^1\Delta$ in nonpolar cyclohexane is an order of magnitude greater than the lifetime in water but approximately half that in highly polar acetonitrile. Likewise, viscosity does not appear to play a prominent role in the radiationless decay of singlet oxygen. While carbon disulfide has *ca.* one-third the viscosity of water, the $^1\Delta$ lifetime is two orders of magnitude *greater* in the former. Similarly, polarizability, ionization potential, and oxygen solubility appear to be unimportant factors in the radiationless decay of singlet oxygen.

There is, however, one solvent property which does correlate well with the $^1\Delta$ lifetime, and this is infrared absorption intensity at 7880 and 6280 cm^{-1}. The theoretical basis of this relationship will be developed in detail in the next section.

2. **Deuterium Effect on the $^1\Delta$ Lifetime.** Although it hardly alters most of the properties of the solvent, we find that deuteration can have a very pronounced effect on the lifetime of singlet oxygen as the data in Table II demonstrate. Photooxidation rate measurement indicate that the lifetime of singlet oxygen is approximately ten times longer in D_2O than in H_2O. Similar large deuterium effects are observed in the water-methanol solvent mixtures. Interestingly deuteration of a solvent does not always lead to a large change in the singlet oxygen lifetime. There is very little difference between the lifetime of singlet oxygen in acetone and perdeuterioacetone. The effect of solvent deuteration on the lifetime of singlet oxygen clearly suggests that C–H and O–H vibrations are somehow important in relaxing singlet oxygen.

The striking deuterium effects on the lifetime of singlet oxygen is an additional salient experimental observation which is accounted for by the theoretical treatment in the following section.

3. **Comparison of Solution and Gas-Phase Quenching of $^1\Delta$.** It is interesting to compare quenching rates in solution with gas-phase values. Reciprocal lifetimes for water and benzene give quenching constants of 5×10^5 and 4×10^4 sec^{-1}, respectively. Gas-phase second-order rate constants for deactivation of $^1\Delta$ have been measured as $\sim 3 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ for both water and benzene.[26]

To compare gas phase and solution quenching, consider the following scheme

$$^1\Delta + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (^1\Delta + Q) \xrightarrow{k_2} {}^3\Sigma + Q$$

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(19) C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **90**, 6233 (1968).

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where k_1 is the rate constant for formation, k_{-1} is the rate constant for dissociation, and k_2 is the first-order quenching constant of the $({}^1\Delta + A)$ collision complex. A kinetic analysis assuming steady-state for $({}^1\Delta + Q)$ and $k_2 \ll k_{-1}$ gives

$$-\frac{d[{}^1\Delta]}{dt} = \frac{k_1k_2}{k_{-1}}[{}^1\Delta][Q] = k_Q[{}^1\Delta][Q]$$

where k_Q is the experimentally observed second-order quenching constant. In the gas phase where the collision frequency is $\sim 10^{11}$ sec^{-1} at 1 M and the estimated pair lifetime is 10^{-12} sec, we find $k_2 \sim 10k_Q$. From the observed gas-phase values for k_Q, we calculate $k_2 \simeq 3 \times 10^4$ sec^{-1} for both water and benzene. To the extent that gas-phase and solution-state collision complexes are the same, k_2 should be the same for both phases.

In solution each singlet oxygen molecule is in constant contact with N nearest-neighbor solvent molecules and we can write $1/\tau \sim Nk_2$. If we estimate N to be 5 for water and 2 for benzene, then from the observed values in solution, k_2 is calculated to be $\sim 10^5$ and $\sim 2 \times 10^4$ sec^{-1} in the respective solvents in reasonable agreement with the values derived from gas-phase data.

Considerations of this nature are not unique to ${}^1\Delta$ but apply to intermolecular deactivation of any molecule when $k_2 \ll k_{-1}$. For example, from the vapor phase rate constant for quenching of ${}^1\Sigma$ oxygen by water[27,28] we can estimate the lifetime of ${}^1\Sigma$ in liquid water to be $\sim 10^{-11}$ sec ($k_2 \sim 2 \times 10^{10}$).

4. Absolute Reaction Rates. Absolute acceptor rate constants and absolute quenching rate constants may now be calculated from published β values for the solvents in which singlet oxygen lifetimes have been measured (refer to Table I). A knowledge of solvent influences on reaction reate constants should be helpful in elucidating reaction mechanisms.

5. Dye Quenching of ${}^1\Delta$. In retrospect, the assumption of Foote and coworkers that the quenching of singlet oxygen by β-carotene is diffusion controlled appears to have been correct. Using their quenching data in a 4:1 benzene–methanol solution[20] and our measured value of $k_Q = 2 \times 10^{10}$ M^{-1} sec^{-1} for β-carotene in benzene (as opposed to their estimate of 3×10^{10} M^{-1} sec^{-1} based on Ware's measurement of oxygen quenching of the fluorescence of naphthalene in benzene),[29] we obtain a ${}^1\Delta$ lifetime of 15 μsec. From the data in Table I a lifetime of 16 μsec can be calculated for this same solvent mixture.

The quenching efficiency of β-carotene can most plausibly be accounted for by a spin-allowed transfer of electronic excitation energy from singlet oxygen to β-carotene, provided the lowest triplet state of β-carotene is either nearly degenerate with or energetically below the ${}^1\Delta$ level. Reactive quenching cannot explain the observed efficiency since β-carotene is not consumed in the quenching process.[20] The observation[30] that oxygen quenches β-carotene triplets with a rate constant of $\sim 10^9$ M^{-1} sec^{-1} does not conflict with the above interpretation, since for low-lying triplets, oxygen quenching by enhancement of intersystem crossing (as opposed to energy transfer from the triplet to produce singlet oxygen) becomes important.[5,31]

Dyes of the type used in Q-switching neodymium lasers exhibit allowed optical absorption in the region of 9000 cm^{-1}.[32] If these dyes have normal singlet–triplet splittings, then they almost certainly have triplet states which lie below ${}^1\Delta$. This is borne out by the high quenching efficiency of the polymethene pyrylium dye, a member of this category.[33] While the quenching constant for I is slightly higher than that for β-carotene, this probably is due to the lower viscosity of the acetonitrile solvent.

Theoretical Section

We noted in the previous section that the lifetime of ${}^1\Delta$ is uncorrelated with most of the common properties of the solvent. There is, however, a striking parallel between the ${}^1\Delta$ lifetime and the intensity of the solvent absorptions near 7880 and 6280 cm^{-1}, resonant with $0 \rightarrow 1$ and ${}^1\Delta \rightarrow {}^3\Sigma$ transitions. This correlation is reminiscent of the electric dipole resonant electronic energy transfer first treated by Förster[34] and expanded by Dexter,[35] except that the present case would require electronic-to-vibrational energy transfer (the conversion of electronic excitation of oxygen into vibrational excitation of the solvent). The substantial deuterium effects observed also suggest that solvent vibrations play a prominent role in the decay of singlet oxygen. At this point we wish to develop the theoretical framework which will permit us to account for the various experimental features of the ${}^1\Delta$ decay and to make predictions regarding the behavior of singlet oxygen in solutions which have not yet been studied.

Radiationless decay in large molecules has usually been treated in terms of a primarily intramolecular mechanism.[36-39] In this approach only small amounts of energy are taken up by indirectly coupled low-frequency vibrations of the medium. In the absence of heavy atom effects relaxation is thus expected to be essentially independent of the nature of the solvent. In contrast to the behavior of large molecules the solvent can be expected to play a major role in radiationless transitions of small molecules, such as oxygen, where internal vibrational modes cannot provide the required set of vibrational states nearly degenerate with the initial state.[38,39]

General Formulation. In our theoretical treatment of the radiationless decay of singlet oxygen we will make use of the general formalism developed by Robinson and Frosch.[36] Radiationless transitions can be considered to arise from interaction of zero-order nonstationary Born–Oppenheimer initial, ψ_i, and final,

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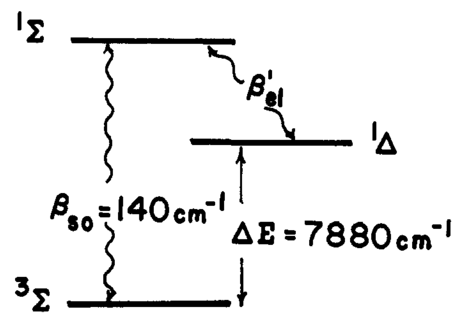

Figure 7. A schematic representation of the coupling scheme responsible for the relaxation of $^1\Delta$ oxygen. β_{so} is a spin–orbit coupling matrix element responsible for coupling the $^1\Sigma$ and $^3\Sigma$ states, and β_{el}' is a matrix element describing the solvent-induced mixing of the $^1\Sigma$ and $^1\Delta$ states.

ψ_f, states under the influence of an interaction Hamiltonian $\mathcal{H}'$. In this approach the rate constant for the transition from the initial state i to a particular final state f may be written as

$$k_{if} = \frac{2\pi}{\hbar\alpha}|\beta_{if}|^2 \simeq \frac{2\pi\tau_{vib}}{\hbar^2}|\beta_{if}|^2 \qquad (4)$$

where α is the energy of interaction between the final state and the molecules of the medium, τ_{vib} is the vibrational relaxation time of the solvent, and $\beta_{if} = \langle\psi_i/\mathcal{H}'/\psi_f\rangle$. If transitions can occur to a number of different final states, then the net quenching rate constant will involve a sum over all possible final states.

With neglect of electron exchange the interaction between O_2 and some solvent molecule with a dipole moment μ can be approximated by

$$\mathcal{H}' = \sum_i \frac{q_i\mu\cos\theta_i}{R_i^2} \qquad (5)$$

where q_i is the charge on an electron or oxygen nucleus located at a distance R_i from the center of the solvent dipole and θ_i is the angle formed between $\mathbf{R}_i$ and $\boldsymbol{\mu}$. If we express wave functions as products of oxygen (ψ) and solvent (Ω) wave functions and substitute the above expression for $\mathcal{H}'$ into eq 2, we obtain the following expression for β_{if}.

$$\beta_{if} = \sum_{mn}\left\langle \psi^0{}_{^1\Delta}\Omega^0 \left| \sum_i \frac{q_i\mu\cos\theta_i}{R_i^2} \right| \psi^m{}_{^3\Sigma}\Omega_n \right\rangle \equiv \sum_{mn}\beta_{mn} \qquad (6)$$

where subscripts on ψ refer to electronic states, and m and n to vibrational levels related by conservation of energy.

Making use of the Born–Oppenheimer separability we can further factor the matix elements and obtain the following expression

$$\beta_{mn} = \beta_{el}F_m^{1/2}\langle\Omega_0|\mu|\Omega_n\rangle \qquad (7)$$

in which

$$\beta_{el} = \left\langle \psi(^1\Delta) \left| \sum_i \frac{e\cos\theta_i}{R_i^2} \right| \psi(^3\Sigma) \right\rangle \qquad (8)$$

where ψ denotes purely electronic oxygen wave functions, Ω_0 and Ω_n are purely vibrational wave functions for the ground electronic state of the *solvent*, and $F_m = |\langle\chi_0(^1\Delta)|\chi_m(^3\Sigma)\rangle|^2$ is the Franck–Condon overlap between the vibrational wave functions, χ, for the specific initial and final electronic states of oxygen indicated. Since $\psi(^1\Delta)$ and $\psi(^3\Sigma)$ are orthogonal and not explicit functions of nuclear coordinates, all terms in β_{el} involving the nuclear coordinates of oxygen will vanish.

From the nature of the electronic wave functions for oxygen,[31] we immediately conclude that in the absence of some spin-dependent perturbation $^1\Delta$ cannot couple with $^3\Sigma$. Consequently, in nonheavy atom solvents there is no solvent-induced *direct* mixing of the $^3\Sigma$ and $^1\Delta$ states. We know from studies of spin–orbit coupling in oxygen, however, that the $^1\Sigma$ and $^3\Sigma$ states are strongly coupled by a matrix element of ~140 cm^{-1}.[40,41] Nonheavy atom solvents can, thus, induce *indirect* mixing of $^1\Delta$ and $^3\Sigma$ by causing mixing of $^1\Sigma$ and $^1\Delta$ states as indicated schematically in Figure 7. Application of second-order perturbation theory[42] to this mixing scheme yields the following modified expression for β_{el}

$$\beta_{el} = \beta_{el}'\frac{\beta_{so}}{\Delta E} \qquad (9)$$

in which

$$\beta_{el}' = \left\langle \psi(^1\Delta) \left| \sum_i \frac{e\cos\theta_i}{R_i^2} \right| \psi(^1\Sigma) \right\rangle \qquad (10)$$

and

$$\beta_{so} = \langle\psi(^1\Sigma)|\mathcal{H}_{so}|\psi(^3\Sigma)\rangle = 140\ \text{cm}^{-1} \qquad (11)$$

For reasons which will become evident, it is desirable to expand μ as is commonly done in treatments of infrared vibrational selection rules[43] and write

$$\mu = \mu_0 + \sum_j\left(\frac{\partial\mu}{\partial Q_j}\right)_{Q_j=0}\cdot Q_j + \ldots \qquad (12)$$

where μ_0 is the permanent ground-state dipole moment of the solvent molecule and Q_j is a normal coordinate. Substituting we obtain

$$\beta_{mn} = \beta_{el}' \times \frac{\beta_{so}}{\Delta E}F_m^{1/2}M_n \qquad (13)$$

where

$$M_n = \left\langle \Omega_0 \left| \mu_0 + \sum_j\left(\frac{\partial\mu}{\partial Q_j}\right)_{Q_j=0}Q_j \right| \Omega_n \right\rangle \qquad (14)$$

When energy is transferred into internal vibrations of the solvent molecules, $n \neq 0$ and thus the term containing μ_0 vanishes due to the orthogonality of the solvent vibronic wave functions.

Using the above expressions, we can express the quenching rate constant as

$$k_{if} \simeq \frac{2\pi\tau_{vib}}{\hbar^2}\left|\beta_{el}' \times \frac{\beta_{so}}{\Delta E}\right|^2 \sum_{mn}F_m|M_n|^2 \qquad (15)$$

Variation of Lifetime with Solvent Infrared Band Intensities. At this point we note that the quantity M_n which appears in the above quenching rate constant expression is the same factor which determines the intensity of $0 \rightarrow n$ transitions of the solvent in the infrared region,[43] and consequently we can obtain M_n directly from spectral data for the solvent.

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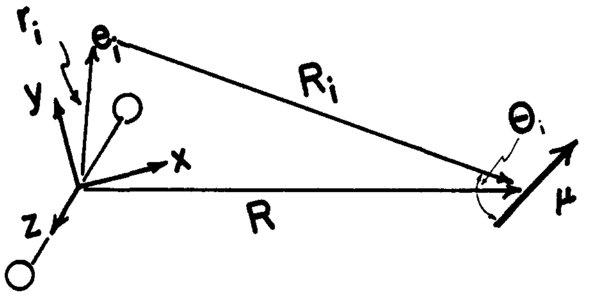

Figure 8. A schematic representation showing the orientation of a solvent molecule with dipole moment μ relative to oxygen at the origin.

The quantity F_m is the Franck–Condon factor for a transition from the 0th vibrational level of the $^1\Delta$ state to the mth vibrational level of the ground $^1\Sigma$ electronic state. Because the potential energy curves for oxygen in its $^1\Delta$ and $^1\Sigma$ state are so similar, both in regard to average internuclear separation (1.207 *vs.* 1.215 Å) and force constants (ω = 1580 *vs.* ω = 1509 cm^{-1}),[44] the Franck–Condon factors decrease extremely rapidly as m increases. For the isolated molecule, the values decrease as $\sim 1:10^{-2}:10^{-4}:2 \times 10^{-7}$ as m increases from 0 to 3.[45] Complete intramolecular conversion of energy from $^1\Delta$ into vibration of $^3\Sigma$ requires excitation to $m = 5$. Because of the rapid decrease in F_m, the relaxation of $^1\Delta$ oxygen is expected to be most rapid when *large* amounts of electronic energy can be transferred to vibrational excitation of the solvent. If, for example, all of the $^1\Delta$ excitation energy is transferred to the solvent, theory predicts that the $^1\Delta$ decay rate will be directly proportional to the solvent ir absorption intensity at ~7880 cm^{-1}. If the solvent absorption bands at this energy are not particularly strong, then quenching in which $^3\Sigma$ is formed in its $m = 1$ vibrational state and the solvent picks up (7880–~1600) cm^{-1} of vibrational excitation will also occur, and solvent absorption in the region of 6280 cm^{-1} becomes important.

Quantitative Test of Theory. It is evident that theory can at least qualitatively account for the dramatic variation of the life-time of singlet oxygen in various solvents and for the fact that there is a good correlation between infrared absorption intensity and quenching rate constants. As a quantitative test of the theory, let us try to compute the lifetime of $^1\Delta$ in a particular solvent. Since experimental values of M_n are available, the only quantity that we will actually have to compute at this point is β_{el}'. To do this, we choose a coordinate system with an oxygen molecule at its center and the z axis as the molecular axis as illustrated in Figure 8.

Noting that $\mathbf{R} = \mathbf{R}_i + \mathbf{r}_i$ or $R_i^2 = (R^2 - r_i^2)$, where r_i is the distance of the ith oxygen electron from the origin, we can write

$$\mathcal{H}' = -\sum_i \frac{e\mu \cos \theta_i}{R^2[1 - (r_i/R^2)]} \qquad (16)$$

A Maclaurin series expansion of $[1 - (r_i^2/R^2)]^{-1}$ yields

$$\mathcal{H}' = -\sum_i \frac{e\mu \cos \theta_i}{R^2}\left(1 + \frac{r_i^2}{R^2} + \ldots\right) \qquad (17)$$

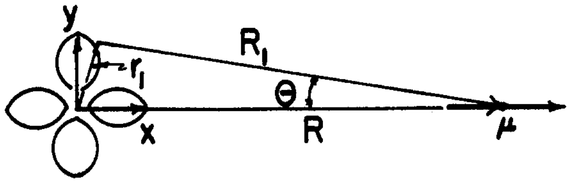

Figure 9. A schematic representation depicting a special orientation of the solvent molecule relative to oxygen. The molecular axis of oxygen is perpendicular to the plane of the paper.

Referring to eq 10 we can write

$$\beta_{\mathrm{el}}' = -\frac{e}{R^2}\sum_i \left\langle \psi(^1\Delta) \middle| \cos \theta_i \left(1 + \frac{r_i^2}{R^2} + \ldots\right) \middle| \psi(^1\Sigma) \right\rangle \qquad (18)$$

If we consider only the outermost pair of oxygen electrons explicitly, then the zero-order electronic wave functions for $^1\Delta$ and $^1\Sigma$ can be expressed in the form[31]

$$\psi(^1\Delta) = \frac{1}{\sqrt{2}}\{|\pi_x(1)\bar{\pi}_x(2)| - |\pi_y(1)\bar{\pi}_y(2)|\}$$
$$\psi(^1\Delta) = \frac{1}{\sqrt{2}}\{|\pi_x(1)\bar{\pi}_y(2)| - |\bar{\pi}_x(1)\pi_y(2)|\} \qquad (19)$$
$$\psi(^1\Sigma) = \frac{1}{\sqrt{2}}\{|\pi_x(1)\bar{\pi}_x(2)| + |\pi_y(1)\bar{\pi}_y(2)|\}$$

where π_x and π_y are antibonding π orbitals occupied by unpaired electrons (1) and (2) and a bar indicates spin β. From the character of these functions it is evident that only interactions involving the unpaired electrons will be effective in mixing, and that a one-electron perturbation of the form $V = V(1) + V(2)$ which destroys axial (z) symmetry will suffice, since

$$\langle\psi(^1\Delta)|V|\psi(^1\Sigma)\rangle = \frac{1}{2}\{\langle\pi_x(1)|V(1)|\pi_x(1)\rangle + \langle\pi_x(2)|V(2)|\pi_x(2)\rangle - \langle\pi_y(1)|V(1)|\pi_y(1)\rangle - \langle\pi_y(2)|V(2)|\pi_y(2)\rangle\} \qquad (20)$$

In the present situation $V(1)$ and $V(2)$ have the same form and we can write

$$\beta_{\mathrm{el}}' = \langle\pi_x|V(1)|\pi_x\rangle - \langle\pi_y|V(1)|\pi_y\rangle \qquad (21)$$

$$V(1) = -\frac{e}{R^2}\cos \theta_1\left(1 + \frac{r_1^2}{R^2} + \ldots\right) \qquad (22)$$

To make a crude estimate of the magnitude of β_{el}', consider the special situation in which the solvent dipole points along the x axis as in Figure 9. Using only the first term in (22) we have

$$\beta_{\mathrm{el}}' = -\frac{e}{R^2}(\langle\pi_x|\cos \theta_1|\pi_x\rangle - \langle\pi_y|\cos \theta_1|\pi_y\rangle) \qquad (23)$$

For an electron in the π_x orbital $\cos \theta_1 \simeq 1$, while in the π_y orbital $\cos \theta_1 = (1 - \sin^2 \theta_1)^{1/2} \simeq 1 - (Y_1^2/2R^2)$. Thus

$$\beta_{\mathrm{el}}' \simeq -\frac{e}{2R^4}\langle\pi_y|Y_1^2|\pi_y\rangle \qquad (24)$$

Using R = 5 Å and $\langle\pi_y|Y_1^2|\pi_y\rangle$ = 1 Å^2, we obtain $\beta_{\mathrm{el}}' \simeq 4 \times 10^3$ esu/cm^2 and $\beta_{\mathrm{el}} \simeq -80$ esu/cm^2. The contribution to β_{el}' from the r_1^2/R^2 term in $V(1)$

[44] G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950.

[45] M. Halmann and I. Laulicht, *J. Chem. Phys.*, 43, 438 (1965).

will be reduced by approximately an order of magnitude. Consequently, our neglect of this term and other higher order terms is justifiable.

The interaction matrix element can now be expressed as

$$\beta_{mn} \simeq 80\ (\text{esu/cm}^2)F_m^{1/2}M_n \tag{25}$$

If we assume the O–O oxygen transition (for which $F_0 \sim 1$) to be most important, then $|M_n|^2$ can be obtained from the solvent infrared absorption intensity in the region of 7880 cm^{-1} through use of the relationship[46]

$$|M_n|^2 = \frac{10^{-38}}{\bar{\nu}}\int \epsilon d\bar{\nu} \tag{26}$$

The molar extinction coefficient for water at 7880 cm^{-1} is $\simeq 10^{-2}$. Integrating over 200 cm^{-1} (kT) gives $|M_n|^2 \simeq 2 \times 10^{-42}$ esu^2 cm^2, from which we calculate $\beta_{0n} \simeq -10^{-19}$ erg $\simeq -5 \times 10^{-4}$ cm^{-1}. Finally, assuming $\tau_{\text{vib}} \simeq 10^{-11}$ sec,[36] we obtain a value for the rate constant for the radiationless decay of singlet oxygen in water of

$$k_{\text{if}} \simeq \frac{2\pi\tau_{\text{vib}}|\beta_{0n}|^2}{\hbar^2} \simeq 6 \times 10^5\ \text{sec}^{-1} \tag{27}$$

In view of the approximations, the agreement with the experimental estimate of $k_2 \simeq 10^5$ sec^{-1} is remarkably good. We have considered a particularly favorable orientation of the solvent dipole relative to the oxygen molecule and the average orientation would not produce as strong an interaction. On the other hand, at the small distances considered the dipole approximation is not strictly valid and leads to an underestimation of β_{el}'. A more accurate, but involved treatment would require a consideration of the electrostatic interaction of a system of point charges.

In order to properly include the effects of the $0 \rightarrow 1$, $0 \rightarrow 2$, and other nonadiabatic transitions, we need the Franck–Condon factors appropriate to each. Isolated molecule Franck–Condon factors are probably not appropriate for oxygen molecules in solution, since there are experimental data which indicate that these may be rather sensitive to solvent perturbations. For example, Evans has observed $0 \leftarrow 0:0 \leftarrow 1$ intensity ratio of $\sim$1:0.3 for the $^1\Delta \leftarrow {}^3\Sigma$ absorption of oxygen at high pressure in 1,1,2-trichlorotrifluoroethane.[47] If we assume that in the present situation $F_1 \simeq 0.1$ (intermediate between the isolated molecule and high pressure cases), then with reference to the data in Tables I and II we obtain the following empirical expression relating the $^1\Delta$ lifetime to solvent ir absorption.

$$\frac{1}{\tau}\ (\mu\text{sec})^{-1} \simeq 0.5(\text{OD}_{7880}) + 0.05(\text{OD}_{6280}) + \text{higher terms} \tag{28}$$

where OD$_{7880}$ and OD$_{6280}$ are optical densities of 1 cm of solvent at 7880 and 6280 cm^{-1}, respectively.[48]

Examination of the data in Tables I and II indicates that for most solvents higher terms in expression 28 can be neglected. Lifetimes in benzene, chloroform, carbon disulfide, and carbon tetrachloride, however, are substantially shorter than those calculated using only the 0–0 and 0–1 terms, but the correlation can be improved by inclusion of terms involving transitions to higher vibrational levels of $^3\Sigma$. The $0 \rightarrow 2$ $^1\Delta \rightarrow {}^3\Sigma$ transition energy is $\simeq$4700 cm^{-1}. Benzene has a very strong absorption in this region (OD of 1 cm $\simeq$7.0). A Franck–Condon factor of $F_2 \simeq 5 \times 10^{-3}$ (*vs.* 10^{-4} for an isolated oxygen molecule) would bring the predicted and observed $^1\Delta$ lifetimes in benzene into good agreement. Chloroform and carbon disulfide exhibit moderate absorption within $\simeq kT$ of 4700 cm^{-1}, and thus radiationless decay of $^1\Delta$ to the $m = 2$ level of $^3\Sigma$ is expected to be important in these solvents also. Of the remaining solvents studied only acetone shows an absorption at 4700 cm^{-1} which is strong (OD $\simeq$ 3.0 in a 1-cm cell) relative to that at 7880 and 6280 cm^{-1}. With an F_2 of 5×10^{-3} the value of τ in acetone calculated from expression 28 is closer to the measured lifetime. Transitions further into the infrared evidently must be included to account for the $^1\Delta$ lifetime in carbon tetrachloride.

When oxygen Franck–Condon factors in various solvents become available, more accurate calculations of radiationless decay rates will be permitted. Singlet oxygen lifetimes are expected to be longest in solvents such as nitrogen and argon which lack infrared intensity. It is worth noting that for a particularly strong solvent–oxygen interaction, transitions to the $m = 5$ vibrational level of $^3\Sigma$ may become more allowed. Hence transfer of excitation energy to the solvent would be less important, and the static dipole moment of the solvent could become significant in radiationless decay.

Deuterium Effects. Since the infrared overtone bands of common solvents in the regions of interest are usually due to C–H or O–H vibrations, the theory predicts that there can be large solvent deuterium effects on the lifetime of singlet oxygen. The lifetime of $^1\Delta$ in water is 2 μsec, and a comparison of the infrared absorption intensities of H_2O and D_2O (Table II) suggests that the lifetime in the latter solvent should increase by approximately a factor of 9. Our experimental studies of the photooxidation efficiencies in H_2O and D_2O indicate that there is actually a tenfold change.[16] A similar tenfold increase in the singlet oxygen lifetime is predicted, and observed, in going from a 1:1 mixture of $H_2O:CH_3OH$ to $D_2O:CD_3OD$.

Solvent deuteration will not necessarily lead to an increase in the lifetime of singlet oxygen as the case of acetone illustrates. The reduction in absorption intensity at 7880 cm^{-1} upon deuteration of acetone is almost completely compensated for by the intensity increase at 6280 cm^{-1}. Although deuteration will in general lead to a decrease in near-ir absorption intensities, it is possible that a situation might arise in which deuteration shifts would create resonances that would actually enhance $^1\Delta$ relaxation.

Because deuteration involves a very minor perturbation of the solvent, the deuterium effect on the lifetime of singlet oxygen can be used as a powerful diagnostic tool for investigating the role of singlet oxygen in various chemical and physical processes. Recently, for example, we have used the deuterium effect to dem-

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[46] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, p 9.

[47] D. F. Evans, *Chem. Commun.*, 367 (1969).

[48] The previous theoretical treatment indicates that k_{if} will be proportional to oscillator strength multiplied by the number of coupled solvent oscillators or roughly to optical density.

onstrate that the methylene blue sensitized photooxidation of tryptophan occurs *via* reaction with singlet oxygen.[16,49] This technique should have widespread application in areas such as photodynamic action.

Order of magnitude increases in the $^1\Delta$ lifetime upon deuteration are predicted for methanol and chloroform and are consistent with some preliminary experimental observations. Thus, these will also be useful solvents for characterizing singlet oxygen reactions.

Heavy Atom Effects. Since the $^1\Delta \rightarrow {}^3\Sigma$ transition is formally spin forbidden, one might have expected to observe large external heavy atom solvent effects on the relaxation rate. Our theoretical analysis indicates that this may not be the case, however, in the relaxation of $^1\Delta$ for the following reason. There is a large spin–orbit mixing of the $^1\Sigma$ state with the $^3\Sigma$ ground state, and mixing of $^1\Delta$ with $^3\Sigma$ is indirectly achieved by an electrostatically induced mixing of $^1\Delta$ with $^1\Sigma$. In order for there to be a specific heavy atom solvent effect on the relaxation, the heavy atoms would have to provide some new route for mixing $^1\Delta$ and $^3\Sigma$. An entirely similar process is responsible for the external heavy atom enhancement of the radiationless relaxation of an excited triplet-state molecule to its ground state, and we can use triplet data to place an upper limit on the importance of this mechanism in the oxygen case. For many of the aromatic hydrocarbons in a bromine-containing solvent (tetrabromozene), the radiative lifetimes are on the order of 50 msec and nonradiative transition rates are estimated to be much smaller than 10^2/sec.[50] If we assume that similar electronic matrix elements will be obtained in the case of oxygen, then heavy atom solvents are not expected to enhance the relaxation of $^1\Delta$, since nonheavy atom solvents already give relaxation rates of $\sim 10^5$/sec.

Amine Quenchers. The amines and other molecules with low ionization potentials may introduce new mixing routes involving charge-transfer states. As developed, our theory does not include this effect, but it could be extended to treat such cases.

Relation between Quenching of $^1\Sigma$ and $^1\Delta$. In spite of the large spin–orbit coupling of $^1\Sigma$ and $^3\Sigma$, direct relaxation of $^1\Sigma$ to $^3\Sigma$ is expected to be small because of the extremely unfavorable oxygen Franck–Condon factors for those $^1\Sigma \rightarrow {}^3\Sigma$ transitions which coincide with solvent infrared bands of measurable intensity. The β_{el}' used in our treatment of $^1\Delta$ relaxation is precisely (without reduction by $\beta_{\mathrm{so}}/\Delta_{\mathrm{E}}$) the quantity which determines relaxation of $^1\Sigma$ to $^1\Delta$, and thus it can be used to compute the rate constants for quenching of $^1\Sigma$ by various solvents. As in the relaxation of $^1\Delta$ to $^3\Sigma$, we expect relaxation of $^1\Sigma$ to $^1\Delta$ without energy transfer to the solvent to be hindered by the small Franck–Condon factors. For the adiabatic $^1\Sigma$ to $^3\Sigma$ transition the solvent will have to take up approximately 5200 cm^{-1} of vibrational excitation. For water the molar extinction coefficient in this region is ~ 1.0 from which we calculate a value of $\beta_{0n} \simeq 0.4\ \mathrm{cm}^{-1}$. Substitution of this value into eq 27 gives a value of $k_{\mathrm{if}} \simeq 3 \times 10^{10}\ \mathrm{sec}^{-1}$ for the quenching rate constant of water which should be compared with our earlier estimate from experimental data of $k_2 \simeq 2 \times 10^{10}\ \mathrm{sec}^{-1}$.

Application to Other Systems. Radiationless decay of other simple molecules may also fall within the scope of the present theoretical treatment. Molecules with low-lying excited states for which $|M_n|^2$ for the solvent is large in regions of favorable F_m would be the most likely candidates. Cases intermediate between the small molecule limit and the primarily intramolecular relaxation characteristic of large molecules may also exist.

The solvent dependence of radiationless decay of $^1\Delta$ is similar to that for europium(III) which was recently characterized in detail by Hass and Stein.[51] Preliminary studies[52] suggest that radiationless transitions in rare earth ions are another system to which the above theory might be applied.

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