Nonradiative Relaxation of Singlet Oxygen in Solution[1]

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Abstract: The solvent induced nonradiative relaxation of singlet oxygen ($^1O_2$, $^1\Delta_g$) was examined by directly monitoring its infrared phosphorescence following pulsed laser generation. The effects of solvent electronic properties, nuclear spin, oxygen isotope, temperature, and magnetic field were examined systematically. It was found that the quenching of $^1O_2$ is related to the energy of the solvent highest frequency mode vibration. A relaxation mechanism based on exchange energy transfer is proposed to accommodate the results. An empirical relationship is developed that permits calculation of the $^1O_2$ lifetime in nonreactive organic solvents.

Singlet oxygen ($^1\Delta_g$, $^1O_2$) is the lowest energy electronically excited state of the most common oxidizing agent. The existence of $^1O_2$ has been known for the past 60 years,[2] but it is only in the past two decades that its important role in chemical and biochemical oxidations has been recognized. The investigation of $^1O_2$, led by Khan and Kasha, Ogryzlo, Foote, and Corey in the early 1960's,[3] has blossomed and matured. Many reactions of $^1O_2$ have been described and explored for synthetic utility and for mechanistic definition.[4] The physical properties of $^1O_2$ in the gas phase and in solution have been investigated. In these studies the nonradiative relaxation of $^1O_2$ caused by its interaction with surrounding bath or solvent molecules has been a topic of particular interest and importance. Several theories have been proposed to account for the unusual sensitivity exhibited by $^1O_2$ to the specific chemical structure of physical quenchers.[5,6] To test these theories we have systematically explored the effect of the electronic character and isotopic substitution of the solvent quencher, the consequences of the nuclear spin and mass of O_2, and the influence of external parameters such as temperature and applied magnetic field on the lifetime of $^1O_2$ in solution. The results of these studies reveal that none of the theories yet proposed can reliably account for the wide-ranging effects that are observed.

The first estimates of the lifetime of $^1O_2$ in solution were based on measurements of its reactivity under steady-state conditions.[7] Later, indirect time-resolved techniques introduced by Wilkinson and Adams,[8] and used by Young[9] and by Kearns,[5] provided values for the lifetime based on the consumption of an added reagent. More recently, direct determination of the $^1O_2$ lifetime has become possible by detection of its emission in solution.[1,6,10]

As is true in principle for all excited states, there are two general routes for deactivation of $^1O_2$. The radiative route is accompanied by emission of infrared light at ca. 1270 and ca. 1590 nm corresponding to the 0 → 0 and 0 → 1 transitions, respectively.[11]

Table I. Lifetime of $^1O_2$ in Halogen-Substituted Benzenes[a,b]

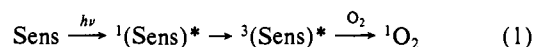| solvent	τ, μs	solvent	τ, μs
C_6H_6	32	$1,3\text{-}C_6H_4F_2$	62
C_6H_5F	49	$1,3,5\text{-}C_6H_3F_3$	99
C_6H_5Cl	51	$1,2,4,5\text{-}C_6H_2F_4$	155
C_6H_5Br	50	C_6HF_5	317
C_6H_5I	35	C_6F_6	3900

[a] All of these lifetimes were obtained using TPP as sensitizer. [b] The lifetimes of $^1O_2$ in some of these solvents obtained by indirect and direct techniques have been reported previously.[1,6,8–10] In these cases there is no significant difference between our value and that obtained by others directly monitoring the phosphorescence.

This phosphorescence competes with nonradiative routes that convert the excitation energy of $^1O_2$ (23 kcal/mol) eventually to heat. In the gas phase at very low pressure the radiative route dominates and is relatively easy to detect.[12] In solution the nonradiative routes account almost totally for the relaxation of $^1O_2$. Consequently, observing the infrared emission under these conditions requires extremely sensitive detectors and sophisticated signal processing. Nevertheless, Krasnovsky[13] reported the first measurement of the 1270-nm emission in solution, and shortly thereafter Khan and Kasha[14] confirmed this result. Detection of the ca. 35-fold weaker 1590 nm emission was reported first by Khan,[11b] and then independently by Salokhiddinov and co-workers,[11a] who also measured the lifetime of $^1O_2$ by resolving the time dependence of the decay of the phosphorescence. We have used this direct approach to measure quantitatively the physical quenching of $^1O_2$ in solution.

Results

(A) Generation and Detection of $^1O_2$ in Solution. It is well-known that irradiation of certain sensitizers with light in the presence of oxygen ultimately leads to $^1O_2$ by the route shown in eq 1.[4] Irradiation of sensitizers such as tetraphenylporphyrin (TPP), methylene blue (MB), or rose bengal (RB) with a ca. 25-ns wide light pulse at 532 nm from a frequency doubled Nd–YAG laser in air or oxygen saturated solution gives infrared emission characteristic of $^1O_2$.[15] (Figure 1).

$$\text{Sens} \xrightarrow{h\nu} {}^1(\text{Sens})^* \rightarrow {}^3(\text{Sens})^* \xrightarrow{O_2} {}^1O_2 \qquad (1)$$

The rate of decay of the infrared phosphorescence provides a direct measure of the lifetime of $^1O_2$. We have determined this decay rate under a variety of experimental conditions and find that its value in some cases depends upon the details of the experiment. In particular, in halogenated solvents the lifetime obtained, though clearly first order, is inversely related to the power

(1) Some of these results have appeared in a preliminary report: Hurst, J. R.; McDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065.

(2) Childe, W. H. J.; Mecke, R. *Z. Phys.* **1931**, *68*, 344. Herzberg, G. *Nature (London)* **1934**, *133*, 759. Kautsky, H.; de Bruijn, H. *Naturwissenschaften* **1931**, *19*, 1043.

(3) Khan, A. U.; Kasha, M. *J. Am. Chem. Soc.* **1970**, *92*, 3293. Arnold, S. J.; Kubo, M.; Ogryzlo, E. A. *Adv. Chem. Ser.* **1968**, *77*, 133. Foote, C. S.; Denny, R. W.; Weaver, L.; Chang, Y.; Peters, J. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 139. Corey, E. J.; Taylor, W. C. *J. am. Chem. Soc.* **1964**, *86*, 3881.

(4) For recent reviews see: "Singlet Oxygen"; Wasserman, H. H.; Murray, R. W., Ed.; Academic Press; New York, 1979. "Singlet Oxygen, Reactions with Organic Compounds and Polymers"; Ranby, B.; Rabek, J. F., Ed.; Wiley: New York, 1978.

(5) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244.

(6) Salokhiddinov, K. I.; Byteva, I. M.; Gurinovich, G. P. *Zh. Prikl. Spektosk.* **1981**, *34*, 892.

(7) Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 6233.

(8) Adams, D. R.; Wilkinson, F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 586.

(9) Young, R. H.; Wehrly, K.; Martin, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 5774.

(10) (a) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 2069. (b) Parker, J. G.; Stanbro, W. D. *Ibid.* **1982**, *104*, 2067. (c) Rodgers, M. A. J.; Snowden, P. T. *Ibid.* **1982**, *104*, 5541.

(11) (a) Salokhiddinov, K. I.; Dzhagarov, B. M.; Byteva, I. M.; Gurinovich, G. P. *Chem. Phys. Lett.* **1980**, *76*, 85. (b) Khan, A. U., *Ibid.* **1980**, *72*, 112.

(12) Davidson, J. A.; Ogryzlo, E. A. *Can. J. Chem.* **1974**, *52*, 240.

(13) Krasnovsky, A. A., Jr. *Photochem. Photobiol.* **1979**, *29*, 29. Biofizika **1976**, *21*, 748.

(14) Khan, A. U.; Kasha, M. *Proc. Natl. Acad. Sci. USA* **1979**, *76*, 6046.

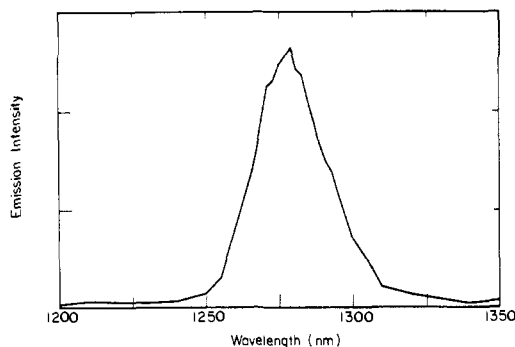(15) The laser and amplifier/detector have been described in detail in supplementary material to the preliminary report.[1]

Figure 1. Emission spectrum of $^1O_2$ in solution recorded 200 μs after irradiation with a 25-ns wide frequency doubled Nd-YAG pulse. The rise time of the detection system is 7 μs.

of the laser pulse used to excite the sensitizer. Similarly, with some sensitizers in polar solvents the $^1O_2$ lifetime also shows a power dependence. The cause of this phenomenon is not known with certainty, but it is reasonably related to generation, by electron transfer from excited sensitizer, of superoxide (O_2^-),[16] or some other odd-electron species,[17,18] capable of rapid and catalytic quenching[19] of $^1O_2$. To avoid complications due to the power dependence, we report lifetimes that are extrapolated to the limit of zero laser power. We find that this procedure gives reliable and reproducible estimates of the lifetime of $^1O_2$. Also, the unanticipated effect of laser power on the $^1O_2$ lifetime may account for the differences that exist between our direct determination and those reported earlier using the indirect technique.

(B) Effect of Solvent Electronic Properties. It is well-known that the lifetime of $^1O_2$ in solution depends critically on the identity of the solvent. A possible cause of part of this dependency is the formation of a complex between $^1O_2$ and the solvent. The strength of the interaction between, for example, a relatively electron rich solvent and $^1O_2$ compared with that of a corresponding electron poor solvent might be reflected in the $^1O_2$ lifetime. To test this possibility we examined $^1O_2$ in a series of aromatic solvents whose properties were varied systematically by incorporation of halogen substituents. These results are presented in Table I.

It is clear from inspection of Table I that the replacement of a hydrogen atom by a halogen atom on benzene affects the lifetime of $^1O_2$ in that solvent. However, it appears that it is the removal of the hydrogen rather that addition of the halogen that is responsible for the effect. Note, for example, that substitution of a single fluorine, chlorine, or bromine atom causes an identical increase in the lifetime of $^1O_2$, even though substituent parameters[20] indicate that these halogens have a significantly different effect on the π-electron donating ability of the solvent. Substitution of an iodine atom causes a relative decrease in the $^1O_2$ lifetime which may be a manifestation of a heavy-atom effect. This point is discussed further below.

The series of fluorinated benzene solvents permits a particularly instructive comparison. The lifetime of $^1O_2$ increases monotonically from 32 μs to 3900 μs as the hydrogen atoms of benzene are sequentially replaced by fluorine atoms. However, as in the previous series, it appears that it is the removal of hydrogen rather than a change in the electronic properties of the solvent caused by substitution that has the greatest effect. This is revealed by analyzing the "effectiveness" of a hydrogen atom in each of these solvents according to eq 2, where τ_{1O_2} is the measured lifetime

$$1/\tau_{1O_2} = k_0 + k_{CH}[C-H] \qquad (2)$$

(16) Cox, S. G.; Whitten, D. G.; Giannotti, C. *Chem. Phys. Lett.* **1979**, *67*, 511. Maillard, P.; Krausz, C.; Giannotti, C.; Gaspard, S. *J. Organomet. Chem.* **1980**, *197*, 285.

(17) A similar suggestion has been made earlier by Ogilby and Foote[18] based on the effect of free radical scavengers on the lifetime of $^1O_2$ in halogenated solvents.

(18) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 1219.

(19) Guiraud, H. J.; Foote, C. S. *J. Am. Chem. Soc.* **1976**, *1984*. Rosenthal, I. *Isr. J. Chem.* **1975**, *13*, 186.

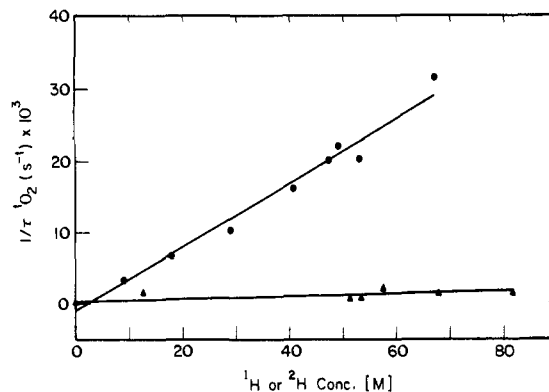(20) Swain, G. C.; Lupton, L. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

Figure 2. The quenching of $^1O_2$ by halogen substituted benzenes and perdeuteriobenzenes at room temperature as a function of the concentration of C-H bonds (circles) or C-D bonds (triangles).

Table II. Lifetime of $^1O_2$ in Deuterated Solvents

solvent	τ, μs	τ_D/τ_H	solvent	τ, μs	τ_D/τ_H
C_6D_6	700	22	$(CD_3)_2CO$	860	17
C_6D_5F	1100	22	D_2O^b	58	13
C_6D_5Cl	1200	23	CD_3OD^b	224	9.6
C_6D_5Br	812	16	CD_3CN	440	7.2
C_6D_5I	277	7.9	$CDCl_3$	640	2.4
$C_2D_5OD^a$	230	24			

^{a} These data are taken from ref 6. ^{b} These data are from the laboratory of Dr. M. Rodgers, Center for Fast Spectroscopy, Austin, TX, ref 10c.

of $^1O_2$ in a particular solvent, k_0 is the rate constant for relaxation of $^1O_2$ in the absence of a specific interaction with a hydrogen atom, k_{CH} is the apparent rate constant for relaxation of $^1O_2$ due to the specific interaction with the aromatic hydrogen atoms, and [C-H] is an effective concentration of aromatic hydrogen atoms bound to carbons obtained by multiplying the number of hydrogen atoms by the molar concentration of the solvent. The data in Table I are plotted according to eq 2 in Figure 2.

The slope of the line in Figure 2 gives k_{CH}. It is remarkable that this value appears to be nearly constant regardless of the number and nature of the other substituents on the benzene nucleus. Moreover, additional data presented below in Figure 4 indicate that k_{CH} is relatively insensitive to even greater changes in the nature of the solvent. Thus it appears that it is some specific property of the carbon-hydrogen bonds in these solvents that determines their quenching ability, and that donor-acceptor interactions of the solvent with $^1O_2$ play little or no role.

(C) Effect of Replacing Hydrogen by Deuterium. The lifetime of $^1O_2$ increases dramatically when all or some of the hydrogen atoms of the solvent are replaced by deuterium atoms. This phenomenon was reported first by Kearns[21] and since then it has been found by us and by others to be totally general for all solvents.[1,6,10,17]

We examined the effect of deuterium substitution on the $^1O_2$ lifetime systematically for a wide range of solvents. The results are summarized in Table II. The first series to note is the halogen-substituted perdeuteriobenzenes. As is observed in the perprotio series, substitution with a fluorine or chlorine atom results in an increase in the $^1O_2$ lifetime in that solvent. However, when an iodine atom, or to a lesser extent, a bromine atom, replaces deuterium, the $^1O_2$ lifetime decreases. The trend in the isotope effects (τ_D/τ_H) reflects the much smaller effect the heavy halogens have in hydrogen atom containing solvents than in their deuterated counterparts.

These findings can be interpreted as a manifestation of the operation of a classical heavy-atom effect[22] on the non-radiative relaxation of $^1O_2$ to ground state triplet oxygen. In hydrogen atom

(21) Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 1029.

(22) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970; p 35.

containing solvents rapid relaxation of $^1O_2$ (k_{CH} large) swamps the heavy-atom effect, and little or none is seen. When all of the solvent hydrogen atoms are replaced by deuterium, the heavy-atom effect is observable because k_{CD} (the apparent constant for relaxation of $^1O_2$ by aromatic carbon–deuterium bonds) is sufficiently small to permit the weak heavy-atom effect to operate.

In this regard, it is important to note that analysis of the data in Table II according to eq 3 (excluding C_6D_5Br, C_6D_5I, and

$$1/\tau^1O_2 = k_0 + k_{CD}[C-D] \qquad (3)$$

CD_3OD) gives a straight line (Figure 2). The slope of this line gives k_{CD}, and as is the case for the analogous hydrogen atom containing solvents, is approximately constant for the range of compounds we have examined. This finding implies that some specific property of carbon–deuterium bonds in these solvents relatively insensitive to specific structure is involved in the nonradiative relaxation of $^1O_2$. The ratio of k_{CH} to k_{CD} from Figure 2 reveals that bonds to hydrogen atoms are about 25 times more effective quenchers of $^1O_2$ than corresponding bonds to deuterium atoms. This finding indicates that the quenching of $^1O_2$ by these solvents is either somehow mass (vibrational frequency) dependent, as has been suggested earlier by Kearns,[5] or, perhaps, nuclear spin dependent. The latter possibility seems unlikely since fluorine atoms, which like hydrogen have spin $^1/_2$, are not effective quenchers of $^1O_2$, Table I. Nevertheless, we examined the possibility that the nuclear spin of the solvent, or of oxygen, somehow influences the nonradiative rate.

(D) Effect of Oxygen Isotope, Nuclear Spin, and External Magnetic Field. It has been noted by several workers that photooxygenation reactions in carbon disulfide solution show unusual effects.[23,24] Kearns, using an indirect technique, reported that the lifetime of $^1O_2$ in CS_2 is 200 ± 60 μs.[24] Our direct measurement of the $^1O_2$ lifetime in CS_2 with TPP as sensitizer reveals a value of 7400 ± 300 μs. The very long lifetime of $^1O_2$ in CS_2 might be traced to the fact that the most abundant isotopes of carbon and sulfur, which account for 95% or more of these nuclei, have nuclear spins of zero. If this is the case, then external, or internal, nuclear spin perturbations might be evident in this solvent. To test this possibility we measured the lifetime of $^1O_2$, in CS_2 and in acetone-d_6, in the presence of a weak external magnetic field. Also, we determined the lifetime of $^1O_2$ enriched in ^{17}O and in ^{18}O in these solvents.

The data reveal that there is no measureable effect of oxygen nuclear spin or oxygen atomic mass on the lifetime of $^1O_2$. The measurements show that $^{17}O_2$ (51% enrichment), $^{18}O_2$ (98% enrichment), and natural abudance $^{16}O_2$ all have the same lifetime of 7600 ± 180 μs in CS_2 and 897 ± 24 μs in acetone-d_6. Similarly, external magnetic fields as high as 4800 G do not affect the lifetime of $^1O_2$. These findings seem to eliminate the nuclear spin difference between hydrogen and deuterium atoms as the cause of their different quenching efficiencies.

(E) Temperature and Quencher Concentration Dependence. One model that has been considered for the solvent-induced nonradiative relaxation of $^1O_2$ requires mixing between the lower lying $^1\Delta_g$ and the somewhat higher energy, $^1\Sigma$ state.[25] The extent of mixing might depend on the solvent's ability to contribute energy to $^1O_2$ and raise it to an excited vibrational level nearly degenerate with the vibrationally relaxed $^1\Sigma$ state.[23] Two mechanisms for the transfer of energy to $^1O_2$ can be envisioned. In the first, a collision between $^1O_2$ and solvent molecule excites a vibration in the solvent which couples to $^1O_2$. In the second, the normal Boltzmann distribution of excited vibrational states of the solvent donate energy to $^1O_2$. For both mechanisms the difference between hydrogen atom and deuterium atom containing solvents could be that it only takes two vibrational quanta of the former to achieve degeneracy with $^1\Sigma$, but the latter requires three quanta. To test for the operation of these mechanisms we examined the tem-
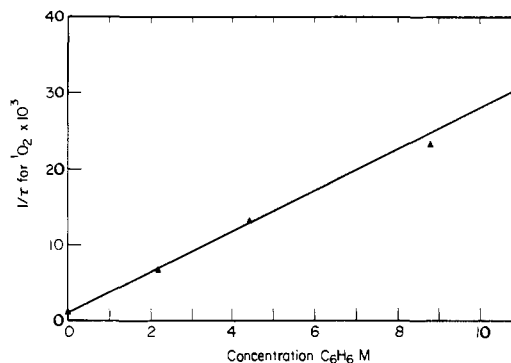

Figure 3. Stern–Volmer quenching of $^1O_2$ in C_6D_6 by C_6H_6 at room temperature.

perature dependence of the $^1O_2$ lifetime and the kinetic order of quenching by hydrogen atom containing solvents.

Using indirect techniques, Koch[26] studied $^1O_2$ in methanol and found little temperature effect, and Kearns obtained a lifetime of $^1O_2$ in chloroform of 60 ± 15 μs at room temperature[24] and observed only a 50% change in the lifetime over a 75° temperature range. Using the direct spectroscopic technique, we obtain a lifetime for $^1O_2$ in chloroform of 250 μs. Thus it is clear that in the earlier determination of the temperature dependence in this solvent, some uncontrolled factor was artificially shortening the observed lifetime. We have examined the temperature dependence of the lifetime of $^1O_2$ over the temperature range from −90 to 37 °C in chlorobenzene, $CHCl_3$, $CDCl_3$, acetone, and acetone-d_6. The results show that temperature plays no significant role in determining the $^1O_2$ lifetime over the range we have examined. This observation eliminates induced nonradiative relaxation mechanisms that depend on utilization of solvent kinetic energy.

If pooling of vibrational energy from several vibrationally excited solvent molecules accounts for the solvent-induced relaxation, then the dependence of the quenching efficiency on concentration would be greater than first order. We examined this possibility by Stern–Volmer analysis of the quenching of $^1O_2$ in deuteriobenzene by benzene. The results of this experiment are displayed in Figure 3. The Stern–Volmer plot is linear, and the slope gives a quenching rate constant of $^1O_2$ by benzene of 2.65×10^3 M^{-1} s^{-1}, which when combined with the concentration of benzene in the pure liquid gives the measured value. This finding eliminates mechanisms that require energy pooling among several solvent molecules to relax $^1O_2$.

Discussion

The results described above show conclusively that $^1O_2$ is relaxed nonradiatively by a specific interaction with the hydrogen atoms of the solvent. This interaction is weakened considerably by replacement of the hydrogens with deuteria, and further by replacement of deuterium with fluorine, for example. The solvent-induced relaxation does not appear to depend strongly on the donor-acceptor properties of the solvent, or on the nuclear spins of the relevant atoms. Furthermore, the solvent is acting as an energy acceptor, rather than a donor, in its interaction with $^1O_2$. These findings point to a relaxation mechanism that features energy transfer from electronically excited oxygen to vibrational levels of the solvent. This suggestion was made earlier by Kearns,[5] who proposed a Förster type dipole-dipole interaction to transfer energy into appropriate overtones of solvent vibrations involving the hydrogen atoms, eq 4. In this equation, β'_{el} and β_{so} are matrix

$$k_q = \frac{2\pi\tau_{vib}}{\hbar^2} \left| \beta'_{el} \times \frac{\beta_{so}}{\Delta E} \right|^2 \sum_{mn} F_m |M_n|^2 \qquad (4)$$

elements that describe the coupling of $^1\Delta$ with $^1\Sigma$ oxygen, and $^1\Sigma$ with $^3\Sigma$ oxygen, respectively. The term F_m accounts for the Franck–Condon factors for transfer to different vibrational levels of ground-state oxygen, and M_n is related to the transition dipole

(23) Foote, C. S.; Peterson, E. R.; Lee, K.-W. *J. Am. Chem. Soc.* **1972**, *94*, 1032.

(24) Long, C. A.; Kearns, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 2018.

(25) The $^1\Sigma$ to $^1\Delta$ 0 → 0 transition occurs at 5280 cm⁻¹.

(26) Koch, E. *Tetrahedron* **1968**, *24*, 6293.

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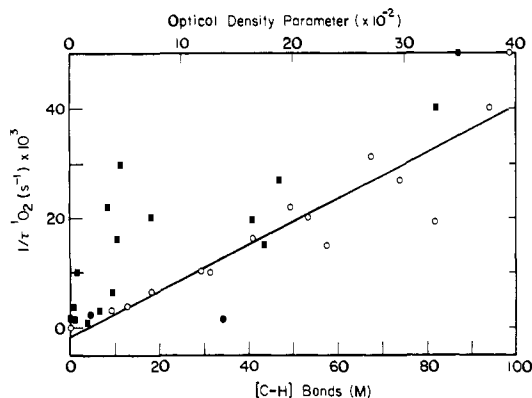
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Figure 4. Reciprocal lifetime of singlet oxygen plotted against the concentration of carbon–hydrogen bonds in the solvent (open circles, lower axis), and against the Kearns optical density parameter (solid squares, upper axis).

of the appropriate solvent overtone vibration. This theoretical treatment was supported by an observed empirical correlation of the $^1O_2$ lifetime with the solvent optical density at 1269 nm (0 → 0 transition of $^1O_2$) and at 1592 nm (0 → 1 transition of $^1O_2$) according to eq 5, where the higher terms were neglected in the

$$1/\tau_{^1O_2} \simeq 0.5 \, (OD_{1269}) + 0.05 \, (OD_{1592}) + \text{higher terms} \quad (5)$$

first approximation. This approach has been adopted by others[6] and expanded in attempts to improve the correlation by substituting the integrated overlap of the $^1O_2$ emission spectrum at 1270 and 1590 nm with the corresponding solvent absorption bands. We propose an alternative mechanism for the solvent-induced relaxation of $^1O_2$ which in some ways is analogous to exchange energy transfer.

Figure 4 is a composite presentation of the dependency of the $^1O_2$ lifetime on the parameter we described above as effective concentration of carbon–hydrogen bonds (open circles), and on the Kearns optical density parameter (solid squares). The line is the least-squares fit to the concentration parameter.

Inspection of Figure 4 reveals that neither parameter predicts the observed lifetime with absolute certainty. However, it is clear that the correlation with hydrogen concentration is the superior of the two. Of course, the two parameters are related. The higher the concentration of carbon–hydrogen bonds, the greater the optical density at the carbon–hydrogen overtone frequencies of 1269 and 1592 nm. The optical density parameters, however, also include a factor derived from the magnitude of the transition dipole (M_n), and it is the inclusion of this part that appears to weaken the observed correlation. This result is in direct conflict with the predictions based on the dipole–dipole energy transfer model.

The exchange mechanism for energy transfer depends on the overlap of vibronic wave functions of the donor and acceptor molecules in much the same way as in the dipole–dipole mechanism. However, exchange transfer is different in that it is independent of the optical transition moments.[27] Exchange energy transfer can be initiated in this system by the normal repulsive interaction of $^1O_2$ and solvent molecules which couples the highest frequency mode of the solvent with a vibronic transition of $^1O_2$. The expectations from this model are expressed semiquantitatively in eq 6. In this equation, Z is a term independent of the specific

$$k_q \simeq Z\sum_{sm} F_s F_m R_{sm} \quad (6)$$

nature of the solvent and contains the matrix elements β'_{el} and β_{so}. F_s is the Franck-Condon factor for a particular (0 → s) vibrational transition of the solvent, F_m is the corresponding factor for the (0 → m) vibronic transition of $^1O_2$ to the ground state, and R_{sm} is related to the energy difference between the oxygen vibronic transition and the appropriate solvent vibrational energy level (an off-resonance factor). We presume that R_{sm} is large for
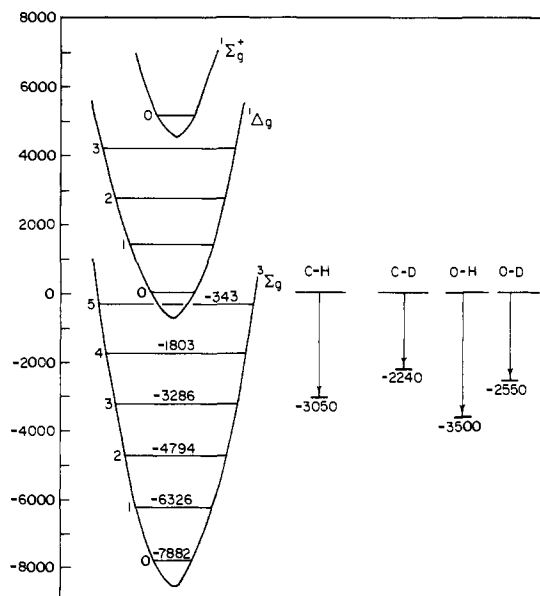
(27) Reference 22, p 539.

Figure 5. The vibronic transitions of oxygen compared to the frequency of the highest energy solvent vibrational mode. Note that the horizontal axis has no particular meaning.

Table III. Quenching of $^1O_2$ by Specific Bonds

highest frequency mode	characteristic[a] frequency, cm^{-1}	k_q, M^{-1} s^{-1} [b]
O-H	3500	2000
C-H	3050	420
O-D	2550	150
C-D	2240	17

[a] The approximate average frequency of the indicated bond over the range of solvents we have explored. [b] These quenching constants come from Figure 2 and Table II. The values of K_{CH} and K_{CD} are derived mainly from aromatic solvents and those for K_{OH} and K_{OD} from water and low molecular weight alcohols. There are more measurements supporting the former pair than the latter. The estimated error is less than ±20% of the reported value in all cases.

exactly resonant energy transfer and becomes increasingly smaller the further from resonance the energy transfer becomes.

This qualitative model is supported by the data if we assign the role of primary energy acceptor to the highest frequency vibrational mode of the solvent, and relegate nonspecific lower frequency modes as acceptors of energy to account for nonresonance between solvent and oxygen levels. An analysis of this proposal is presented in Figure 5.

The potential energy curves in Figure 5 are schematic representations of the lower electronic and vibrational levels of oxygen drawn after Herzberg.[28] The group frequencies assigned to individual quenching bonds are the averages of the experimentally observed fundamental vibrations and are generally the highest frequency mode of the solvent. In the discussion that follows we attempt to explain simply the order of quenching constants reported in Table III. The absolute magnitudes of k_q depend on the specific functional form of R_{sm}, which is unknown.

First, we focus on the fundamental of the solvent highest frequency mode. This, the 0 → 1 transition, has the largest Franck–Condon factor, and moreover it is not necessary to involve overtone or combination bands to explain the results. Inspection of Figure 5 reveals that, for solvents containing carbon–hydrogen bonds, there is a near reasonance (within ca. 200 cm^{-1}) between the $^1O_2$ (0 → 3) transition and the solvent's highest frequency fundamental vibration. In contrast, for solvents containing car-

(28) Herzberg, G. "Spectra of Diatomic Molecules"; Van Nostrand Reinhold: New York, 1950.

bon–deuterium bonds, the $^1O_2$ ($0 \rightarrow 3$) transition is ca. 1050 cm^{-1} more energetic than the solvent's highest frequency fundamental vibration. Thus, the off-resonance factor R_{31} is expected to be larger for the former than for the latter, thereby accounting for the deuterium isotope effect.

Similarly, this model accounts for the larger value of k_q for oxygen–hydrogen bonds than for carbon–hydrogen bonds (Table III). In this case, the fundamental of the oxygen–hydrogen vibration is sufficiently energetic to accept energy from the $0 \rightarrow 2$ vibronic transition of oxygen with ca. 1200 cm^{-1} to be absorbed by low-frequency modes. The $0 \rightarrow 2$ vibronic transition has a considerably larger Franck–Condon factor than the $0 \rightarrow 3$ transition,[29] and this difference can account for the increased quenching ability. The k_q for oxygen–deuterium bonds falls correctly between carbon–deuterium (larger R_{sm}) and carbon–hydrogen (smaller R_{sm}) bonds.

In sum, the predictions from this model for the nonradiative solvent-induced relaxation of $^1O_2$ can be stated simply. The greater the energy of the highest frequency vibrational mode of the solvent, the nearer to resonance is a $^1O_2$ vibronic transition with a large Franck–Condon factor. This view is supported qualitatively by the data and accounts for the observations we have made on the properties of $^1O_2$ in solution.

Finally, our findings show clearly that the major feature controlling the physical quenching of $^1O_2$ in solution is related to the energy of the highest frequency vibrational mode of the solvent (Table III). The apparent second-order quenching rate constants, k_q, increase monotonically, but not linearly, as the frequency of this vibration increases. There are several possible explanations for this phenomenon; the one we favor is based on a simple exchange energy transfer model, which is outlined above. Regardless of the specific details of the mechanism, however, the data in Table III can be used to make reasonably accurate predictions of the lifetime of $^1O_2$ in a particular nonreactive solvent according to eq 7, where M is the molar concentration of the solvent, N_i is the

$$1/\tau_{^1O_2} = M \sum_i N_i k_{qi} \qquad (7)$$

number of times a particular bond to hydrogen (or deuterium) occurs, and k_{qi} is the quenching constant for that bond. The data in Table III provide estimates of k_{qi} for some specific chemical bonds. Recent work by Rodgers[30] provides values for additional examples and generally supports application of eq 7.

Conclusions

Our measurements of the solvent, nuclear spin, and temperature dependence of the lifetime of $^1O_2$ in solution support an exchange energy transfer model more strongly than they do a dipole–dipole interaction. Regardless of the details of the quenching mechanism, however, the development of specific quenching rate constants for individual bonds should prove valuable in the estimation of the lifetime of $^1O_2$ in organic solvents.

Experimental Section

Equipment. The equipment used for the detection of the near-infrared emission of singlet oxygen was described in a previous communication.[1] Visible absorption spectra were taken with a Perkin-Elmer 552 instrument. Infrared spectra were recorded on a Nicolet Model 7199 FTIR. Flourescence spectra were recorded with a Foci Mark I spectrophotometer. Mass spectra were taken with a Varian MAT CH-5.

Materials. Methylene blue and rose bengal (Fisher (Scientific) were used without purification. Tetraphenylporphyrin was purified by the method of Barnett.[31]

m-Difluorobenzene, chlorobenzene-d_5, fluorobenzene-d_5, fluorobenzene, bromobenzene (Aldrich), chlorobenzene (Mallinckrodt), iodobenzene (Eastman), and bromobenzene-d_5 (Stohler Isotopes) were distilled before use. Tetrahydrofuran (Aldrich, gold label) was distilled from Na wire. Acetonitrile (Aldrich, gold label) was distilled from CaH$_2$. Hexafluorobenzene, pentafluorobenzene, 1,2,4,5-tetrafluorobenzene, 1,3,5-trifluorobenzene, benzonitrile, methanol-d (Aldrich), p-dioxane (MCB), benzene (Mallinckrodt), deuterium oxide (Sigma), carbon disulfide (J. T. Baker, spectrophotometric grade), methylene chloride, cyclohexane, chloroform (Burdick and Jackson, distilled in glass), benzene-d_6 (Stohler), chloroform-d, acetonitrile-d_3, acetone-d_6 (Merck), and acetone (Fisher Scientific, spectrophotometric grade) were used without further purification. Carbon tetrachloride (Burdick and Jackson, or Mallinckrodt) was distilled, dried over MgSO$_4$, and/or treated with NaHCO$_3$ (anhydrous), or used without purification. Iodobenzene-d_6 was prepared by the method of Safe[32] and mass spectral analysis showed ca. 97% deuterium incorporation. The lifetimes obtained in this, and the other deuterated solvents, are corrected for residual hydrogen content.

Registry No. Oxygen, 7782-44-7.

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(30) We thank Dr. Rodgers for sending us a copy of his unpublished paper, and for several very productive discussions.

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