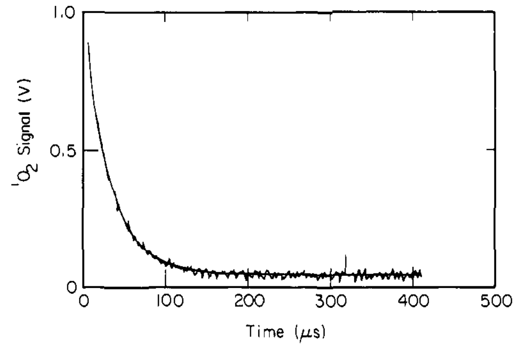

Figure 2. Observed decay of the transient infrared emission following pulse irradiation of tetraphenylporphyrin in benzene. The solid line through the data is the least-squares fit to a first-order decay.

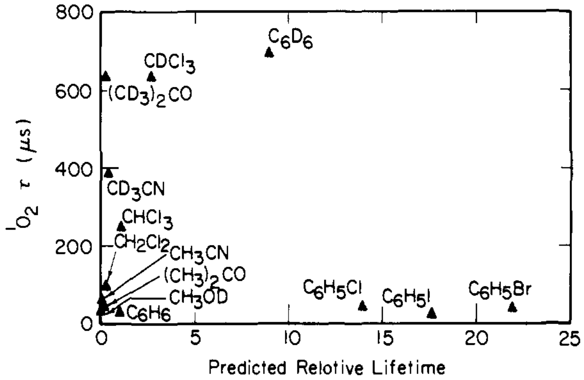

Figure 3. Comparison of the observed lifetime of $^1O_2$ in various solvents to the relative lifetime predicted by the equation used by Salokhiddinov et al.,[7,22] which is based on the overlap of the solvent absorptions with the oxygen emission and various physical properties of the solvent.

under identical conditions at extrapolated time equals zero.

The radiative lifetime of $^1O_2$ in the gas phase at extrapolated zero pressure has been calculated to be 45 min.[17,18] The lifetime of $^1O_2$ in condensed phase is reduced by interaction with the medium. By comparing the intensity of tetraphenylporphyrin (TPP) fluorescence to that of the observed $^1O_2$ emission, Krasnovsky[5] has recently reestimated the quantum efficiency of the phosphorescence of $^1O_2$ in CCl_4 to be ca. 4.4×10^{-3}. Thus it is evident that the rates of the radiative as well as the nonradiative processes are influenced by solvation.

An important factor for understanding the influence of the solvent on the rates of decay of $^1O_2$ is the remarkable increase in lifetime when the solvent is deuterated.[13] Our findings indicate that the effect of deuteration is universal. Indirect determination of the lifetime of $^1O_2$ in acetone and acetone-d_6 by Merkel and Kearns[19] showed no isotope effect. However, our results confirm the recent report by Foote and Ogilby[20] of an isotope effect of 18 ± 4 in this solvent.

A theoretical model advanced by Kearns[19] to explain the effect of solvent on the lifetime of $^1O_2$ assumed an intermolecular electronic-to-vibrational energy transfer which was supported by an apparent empirical correlation of the lifetime with the intensities of the solvent infrared absorptions at 1269 and 1592 nm. Our data, especially the solvent isotope effect in acetone, indicate essentially no correlation with the suggested solvent absorption intensities. Recently Salokhiddinov and co-workers[7] suggested a modification of Kearn's correlation in which the overlap of the complete infrared phosphorescence spectrum of $^1O_2$ with the solvent absorption spectrum and certain other physical properties of the solvent were claimed to predict the relative lifetime of $^1O_2$. Our findings also disagree with the predictions made by this modified approach as is shown in Table I and Figure 3.

Solvation of $^1O_2$ apparently increases the rate of the radiative as well as the nonradiative decay paths. The recent report by Krasnovsky[5] indicates that the radiative rate is independent of the nature of the solvent. This is approximately correct for many of the solvents we have studied. In particular, we find that there is no measurable effect of solvent deuteration on the radiative process. However, when the solvent is an aromatic compound there is an effect on the radiative rate. The data in Table I show that for benzene, deuteriobenzene, and the halogenated benzenes the radiative rate is approximately twice that in the other solvents. While we do not yet have a precise explanation for this effect, it does appear to be related to the polarizability of the sovlent. This observation may indicate the formation of contact complexes between $^1O_2$ and the solvent. If so, these complexes may also affect the nonradiative rate.

In sum, we have developed a procedure to determine reliably the lifetime of $^1O_2$ in solution. Our measurements of the lifetime under a variety of conditions have revealed properties of this system. We are continuing to probe the variables that control the lifetime of $^1O_2$ in solution.

Acknowledgment. We thank Charles Hawley and James Wehmer of this department for their valuable help in selection of the detector, construction of the amplifier, and operation of the laser system. This work was supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Oxygen, 7782-44-7.

Supplementary Material Available: Schematic diagram of the amplifier used with the germanium photodiode (1 page). Ordering information is given on any current masthead page.

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[20] Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 1219.

[21] Quimby, D. J.; Longo, F. R. *J. Am. Chem. Soc.* **1975**, *97*, 5111.

[22] The equation put forth by Salokhiddinov et al.[7] is

$$\tau = cn^4R^6d\Big/\left(\mu\int I\alpha\nu^{-4}\,d\nu\right)$$

where τ = lifetime of $^1O_2$, n = refractive index of the solvent, R = mean radius of the solvent molecule, d = density of the solvent, μ = molecular weight of the solvent, I = intensity of $^1O_2$ emission as a function of ν, α = optical density of the solvent as a function of ν, ν = frequency, and c = a proportionality constant.

Optical Determination of the Collisional Lifetime of Singlet Molecular Oxygen [$O_2(^1\Delta_g)$] in Acetone and Deuterated Acetone

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Received November 2, 1981

Recently Ogilby and Foote[1] have carried out an investigation of the effect of solvent deuteration on the collisional lifetime of singlet molecular oxygen in acetone, acetonitrile, benzene, and chloroform and have observed an order of magnitude increase in all cases. The earlier work of Merkel and Kearns[2] also indicated an order of magnitude lengthening of lifetimes with solvent deuteration for H_2O and chloroform; however, in the case of acetone, a lifetime of 26 μs was obtained for both. These data were consistent with a theory developed by them that related the $O_2(^1\Delta_g)$ quenching rates to infrared absorption of the solvent, primarily at 1.27 and 1.59 μm corresponding to (0,0) and (0,1) $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ transitions. Importance of the (0,1) transition was a consequence of the assumption that the associated Franck-

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[1] P. R. Ogilby and C. S. Foote, *J. Am. Chem. Soc.*, *103*, 1219 (1981).

[2] P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, *94*, 7244 (1972).

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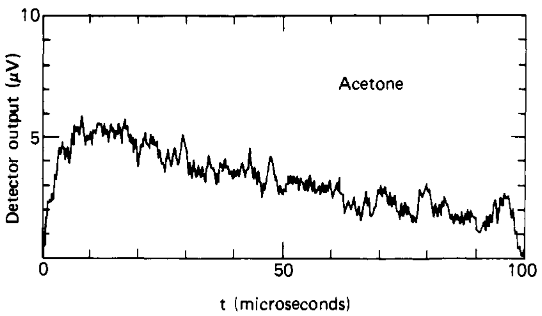

Figure 1. Detector output displayed as a function of the time for an air-saturated solution containing approximately 10^{-5} M free-base hematoporphyrin dissolved in acetone. The spectrometer setting corresponded to a wavelength of 1.27 μ. The time constant obtained from analysis of data was 65.3 ± 5.3 μs.

Condon factor was 0.10, approximately 10 times larger than the value for the isolated molecule, the increase being due to interaction with the solvent. The particular case of acetone is somewhat unique, in that with an assumed Franck–Condon factor of 0.1 for the (0,1) transition the total infrared absorption coefficient (i.e., sum of the 0,0 and 0,1 contributions) is approximately the same for the protiated and deuterated species. Thus the $O_2(^1\Delta_g)$ lifetimes in both solvents should be comparable. Merkel and Kearns used this result to provide key support for their theory.

In carrying out their measurements, Ogilby and Foote used rose bengal as a photosensitizer and relied on use of the acceptors rubrene and 1,3-diphenylisobenzofuran (DPBF) to determine the rate of solvent quenching of $O_2(^1\Delta_g)$ relative to that of the acceptor itself. Two main limitations to the method used by them are (1) it is only possible to obtain ratios of the $O_2(^1\Delta_g)$ lifetimes in the protiated and deuterated solvents and (2) the use of chemical indicators may lead to significant problems in interpretation of the data. In part, the latter difficulty arises due to acceptor quenching at a rate comparable to that of the solvent,[3] a factor that Ogilby and Foote have considered in developing a more sensitive means to monitor acceptor concentration. This involved modulated fluorescence excitation combined with the use of a lock-in amplifier to provide signal-to-noise enhancement. As a consequence they were able to use acceptor concentrations of the order of 10^{-6} M, a factor of 10 smaller than that used by Merkel and Kearns. However, a problem still remained due to the fact that acceptors such as DPBF react with both singlet oxygen and free radicals in the same manner,[4,5] an apparent difficulty encountered by Ogilby and Foote using a chloroform solvent. To resolve these uncertainties, we have carried out direct measurements of the decay times of singlet oxygen in acetone and deuterated acetone using remote optical detection of the collisionally induced emission at 1.27 μm, thus avoiding problems associated with the use of chemical indicators.

Generation of $O_2(^1\Delta_g)$ involved the use of free-base hematoporphyrin (Sigma, catalogue no. H 7253) as a sensitizer at a concentration of approximately 10^{-5} M. In both cases the solutions were air saturated. A Q-switched, frequency-doubled, Nd:YAG laser (Quanta Ray, Model DCR-1) radiating at 5320 Å was used as the excitation source with pulse energies of approximately 10 mJ and a pulse duration of 10 ns. The solution was contained in a 1 cm × 1 cm cuvette placed at the entrance slit (slit width 5 mm) of a Spex Minimate spectrometer. A Corning 7-56 infrared long-pass filter was placed between the entrance slit and the cuvette to eliminate scattered laser light.

Light emerging from the spectrometer exit slit was focused on the 1 mm × 1 mm active area of a Judson J-16 germanium photodiode detector. The detector output signal was then amplified and directed to the input of a PAR 160 boxcar integrator and finally to a strip chart recorder.

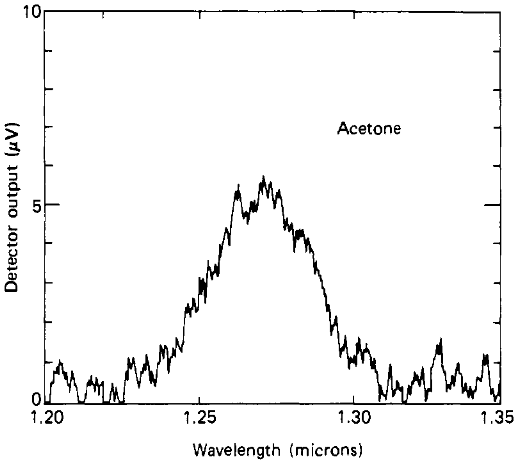

Figure 2. Spectral variation of infrared emission intensity resulting from pulsed-laser irradiation of an air-saturated solution containing approximately 10^{-5} M free-base hematoporphyrin dissolved in acetone. The fact that the maximum emission occurs at a wavelength of 1.27 μ identifies the emitting species as $O_2(^1\Delta_g)$. The scan was carried out with the PAR 160 set on hold with a time delay of 30 μs.

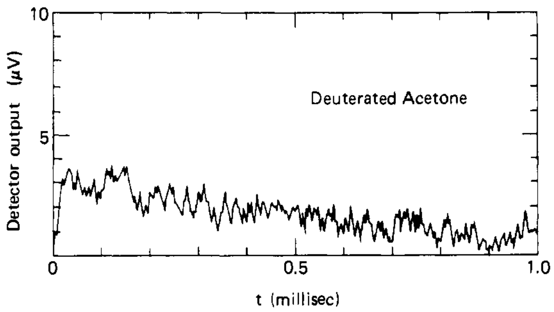

Figure 3. Detector output displayed as a function of time for an air-saturated solution containing approximately 10^{-5} M free-base hematoporphyrin dissolved in deuterated acetone. The spectrometer setting corresponded to a wavelength of 1.27 μ. The time constant obtained from analysis of the data was 838 ± 119 μs.

Results of a run in acetone [Aldrich, 99+%, spectrophotometric grade, Catalogue No. 15, 459-8] appear in Figure 1, in which detector output is displayed as a function of time after initiation of the laser pulse over a 100-μs time interval. The spectrometer setting corresponded to a wavelength of 1.27 μm. The decay constant was obtained from a semilog plot using smoothed values and corresponded to a lifetime of 65.3 ± 5.3 μs. This is much larger than the value obtained by Merkel and Kearns and is somewhat longer than the more recent data of Krasnovsky[6] and Salokhiddinov et al.,[7] both of whom obtained values close to 50 μs. Variation of the detector output resulting from a spectrometer scan over the spectral range from 1.20 to 1.35 μ appears in Figure 2. Maximum emission occurs at 1.27 μm, clearly establishing the source as the collisionally induced $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ radiative transition.

A plot of detector output vs. time for deuterated acetone [Sigma, 99.5 atom % D, catalogue no. A5890] appears in Figure 3, in which the time base has been expanded to 1 ms. Analysis of the data in this case yields a decay time of 838 ± 119 μs, somewhat more than an order of magnitude longer than in acetone. A spectral scan was also carried out, in this case producing a trace essentially identical with that displayed in Figure 2. A final run (not shown) was made to determine the effect of H_2O addition to deuterated acetone. Addition of 5.6% distilled water (by volume) reduced the quenching time to 109 ± 7 μs.

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The results of this investigation are consistent with the findings of Ogilby and Foote and are collectively in disagreement with the theoretical calculations of Merkel and Kearns. A possible means of avoiding this difficulty exists if it is assumed that the associated Franck–Condon factors are negligibly affected by solvent interaction, with the consequence that only 0,0 transitions are important. Under this assumption, we find, using optical density data presented in ref 2, the ratio of lifetimes in deuterated and protiated acetone to be 7.5 and similarly that the ratio for D_2O and H_2O, using corresponding values, is still in order of magnitude agreement with the experimental data.

Acknowledgment. This work was supported by the U.S. Naval Sea Systems Command under Contract N00024-81-C-5301.

Chemistry of Singlet Oxygen. 36. Singlet Molecular Oxygen ($^1\Delta_g$) Luminescence in Solution following Pulsed Laser Excitation. Solvent Deuterium Isotope Effects on the Lifetime of Singlet Oxygen

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Received November 10, 1981

We recently reported that solvent deuterium isotope effects on the lifetime of singlet molecular oxygen ($^1\Delta_g$) were significantly larger than values published by other investigators.[1] Our observations suggested that the original explanation for the quenching of singlet oxygen by solvent interactions was inadequate. We have now determined the lifetime of singlet oxygen in various solvents by direct observation of singlet oxygen phosphorescence at 1270 nm following pulsed-laser excitation of a sensitizer. These observations support our eariler results.

Luminescence from $^1O_2$ ($^1\Delta_g(v = 0) \rightarrow {}^3\Sigma_g^-(v = 0)$) at 1270 nm was first observed in solution by Krasnovski[2] and Kasha and Khan.[3] Studies of the luminescence after flash excitation of a sensitizing dye quickly followed.[4] The experimental approach used in our investigations is similar.[5] The sensitizing dye, excited with a pulsed-laser beam (4 ns peak width at half-height), transfers energy to oxygen from its triplet state to give singlet molecular oxygen ($^1\Delta_g$). Luminescence was characterized as that of singlet oxygen by taking an emission spectrum, by several quenching studies using, in particular, tetramethylethylene and 1,4-diazabicyclo[2.2.2]octane (Dabco),[6] and by noting the decrease in luminescence intensity when an interference filter centered at 1270 nm was replaced by one centered at 1300 nm.[5] Since singlet oxygen is formed essentially instantaneously (on a microsecond timescale), its decay should follow simple first-order kinetics. First-order plots of the data are indeed linear (Figure 1), confirming the kinetic suppositions, and directly yield the lifetime of singlet oxygen. Table I lists values for the lifetime of singlet oxygen determined by this technique[7] along with the values re-

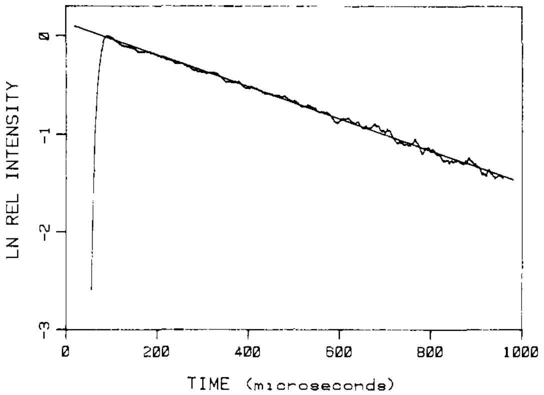

Figure 1. Semilog plot of the decay of singlet oxygen luminescence following laser-flash excitation of mesoporphyrin IX dimethyl ester (2.8×10^{-5} M) in acetone-d_6.

Table I. Lifetime [$\tau(^1O_2)$] of Singlet Molecular Oxygen ($^1\Delta_g$) in Solution (μs)

	lit values		
solvent	determined indirectly	determined directly	this work
acetone	26.3 ± 7.0,[a] 42.0 ± 8.0,[c] 55.0 ± 1.3[f]	50,[j] 51 ± 5[q]	46.5 ± 2.0
acetone-d_6	602–1042,[f] 26[b]		690 ± 20
acetonitrile	30.3 ± 6.8,[b] 57.0 ± 9.0,[c] 92 ± 5[f]		54.4 ± 1.3
acetonitrile-d_3	885–2128[f]		600 ± 33
benzene	23.8 ± 6.5,[b] 27 ± 4,[c] 24.4 ± 2.4,[l] 25.6 ± 2.5,[n] 28.2 ± 0.4[f]	30 ± 4[q]	26.7 ± 1.3
benzene-d_6	36.0 ± 7.0,[m] 740–1540,[f] 500–1000[f]		550 ± 11
D_2O	33.3 ± 2.1,[o] 35.7 ± 2.0,[o] 53 ± 5,[d] 42 ± 5,[p] 53 ± 3,[e] 120[k]	100[j]	68.1 ± 2.5

[a] Reference 8a. [b] Reference 8. [c] Reference 9. [d] Reference 10a. [e] Reference 10b. [f] Reference 10c, maximum range of values reported. [j] Reference 12. [k] Reference 12b. [l] Reference 13a. [m] Reference 13b. [n] Reference 13c. [o] Reference 14a. [p] Reference 14b. [q] Reference 4.

Table II. Solvent Deuterium Isotope Effects on the Lifetime of Singlet Molecular Oxygen ($^1\Delta_g$) in Solution

solvent	$k_{decay}^{H}/k_{decay}^{D}$[a] (this work)	$k_{decay}^{H}/k_{decay}^{D}$[b]
acetone	14.8 ± 1.1	19.9 ± 1.3, 17.0 ± 3.8, 17.8 ± 2.0
acetonitrile	11.0 ± 0.9	8.7 ± 1.0, 7.2 ± 1.6
benzene	20.6 ± 1.4	15.9 ± 2.1, 16.8 ± 1.0[c]

[a] This work. [b] Reference 1. [c] Contained 0.8% (by volume) MeOH in order to dissolve methylene blue. With the pulsed-laser technique, addition of a comparable amount of MeOH to the system shortens the lifetime of singlet oxygen in benzene-d_6 sufficiently to yield an isotope effect of approximately 16.

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

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(5) Sensitizing dyes were excited with either the second or third harmonics of a Quanta-Ray (DCR-1) Nd:YAG laser. A Schott KG-3 filter removed any residual fundamental radiation at 1064 nm. An interference filter (Oriel, 51% transmittance at 1270 nm, 5-nm width at half-height) isolated oxygen luminescence before it was focused through a Schott RG-850 cutoff filter onto an intrinsic germanium photodiode. Diodes of varying surface areas (Judson Infrared, Inc.) were used with preamplifiers whose rise times and sensitivities likewise varied. The resultant signal was digitized by a Biomation Model 805 waveform recorder, averaged with a computer built by Drs. J. V. V. Kasper and G. Gust and analyzed on a PDP 11/45 computer using programs written by P. R. Ogilby and Dr. J. V. V. Kasper. The intensity of luminescence decreased significantly when an interference filter (Oriel, 40% transmittance at 1300 nm, 5-nm width at half-height) was used. By monitoring luminescence intensity as a function of wavelength (uncalibrated Bausch and Lomb grating monochromator blazed at 675 grooves/mm), an emission spectrum for $^1O_2$ in solution was obtained.[6] λ_{max} ($\sim$1277 nm) is slightly red shifted from values reported elsewhere.[3]

(6) Ogilby, P. R.; Foote, C. S., to be submitted for publication.

(7) Several dyes were used to allow sufficient solubility in the various solvents. For most of the work, *meso*-porphyrin IX dimethyl ester (Sigma) was used. Mesotetraphenylporphine (Aldrich), 1,8-dinaphthalene thiophene (K and K laboratories), Rose Bengal (Eastman), and thionine hydrochloride (Eastman) were also used, the latter two in D_2O. Mallinckrodt protiated spectrograde solvents were used. No effect was observed when the solvent was stored over molecular sieves. Deuterated solvents were obtained from Aldrich (acetone, acetonitrile), KOR (benzene), and Stohler (D_2O).[1] A slight decrease ($\sim$20%) in the lifetime of singlet oxygen occurred when deuterated solvents were stored over molecular sieves. For most of the experiments, solutions were air saturated. No difference was seen in the lifetime upon oxygen saturation of the solution.

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