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.

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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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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-

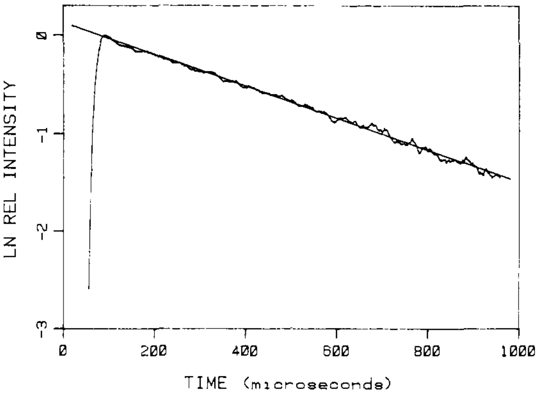

Figure 1. Semilog plot of the decay of singlet oxygen luminescence following laser-flash excitation of mesoporphyrin IX dimethyl ester (2.8 × 10^{-5} M) in acetone-d_6.

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

solvent	lit values: determined indirectly	lit values: 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	$k_{\mathrm{decay}}^{\mathrm{H}}/k_{\mathrm{decay}}^{\mathrm{D}}$[a] (this work)	$k_{\mathrm{decay}}^{\mathrm{H}}/k_{\mathrm{decay}}^{\mathrm{D}}$[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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[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] $\lambda_{\max}$ (~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 (~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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ported by other investigators. The usual methods for determination of singlet oxygen lifetimes in solution are indirect and involve monitoring the loss of a singlet-oxygen acceptor. The kinetics of this approach are often complicated and require that various simplifying assumptions be made. Lifetime values determined by using this approach are also reported in Table I.

From the observed values for the lifetime of singlet oxygen in protiated and deuterated solvents, values for the solvent isotope effect are calculated and compared to values independently determined[1] (Table II). Agreement between the values is as good as can be expected, considering the limitations of the indirect method.

In the course of this work it was discovered that high sensitizer concentrations or high laser powers can yield lifetimes that are much lower than those measured under other conditions.[12a,15] This effect is particularly important for solvents in which the lifetime of singlet oxygen is long. Values for the lifetime of singlet oxygen determined at high dye concentrations or at high laser powers can be extrapolated to zero concentration and power; values so obtained do not differ significantly from those in Table I. It seems likely that multiphoton processes (or interaction of multiple excited species) can result in the creation of species that quench singlet oxygen (e.g., the reduction of $^3O_2$ to yield $O_2^{-}\cdot$). For the porphyrins it is known that ionization potentials are low and that Rydberg states are readily populated.[16] Photooxygenation of dye molecules also appears to create species that quench singlet oxygen.[15] Absorption spectra of some dyes taken after irradiation show changes; in particular, extensive reaction of dyes occurred in $CHCl_3$ and CCl_4. We showed previously that species other than singlet oxygen (perhaps radical reactions) complicate the reactions in chloroform.[1] A more complete discussion is presented elsewhere.[6,17]

The large values of the deuterium isotope effect observed confirm our suggestion that the approach taken by Kearns[8b] does not provide an adequate description for the quenching of singlet oxygen by solvent interactions. In the present case, a *quantitative* correlation was not found between singlet oxygen lifetimes and the optical density of the solvent in regions that correspond to the transitions [$^1\Delta_g(v = 0) \rightarrow {}^3\Sigma_g^-$] where $^3O_2$ is formed with varying numbers of vibrational quanta. A more complete development is presented elsewhere.[6,17]

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Protonation of 11-Methylene-1,6-methano[10]annulene[1]

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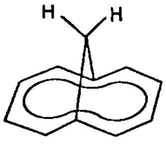
The bridged monocyclic 10-π-electron 1,6-methano[10]annulene[2] (**1**) is a classic example of Hückel aromaticity[3] despite its strong transannular interaction.[4,5,7] An important contribution to the high reactivity of **1** toward electrophiles[3b] may be the transannular interaction in the Wheland intermediate.[8] In continuation of our studies on the σ complexes of **1** under stable ion solution conditions[8,9] we now report on the protonation of 11-methylene-1,6-methano[10]annulene (**2**).[10]



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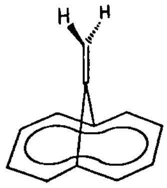

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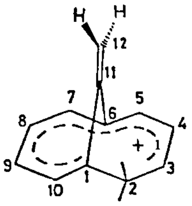

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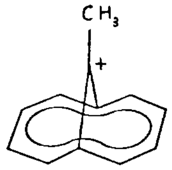

4

The intriguing aspect of **2** is that it contains a 10-π-electron aromatic system with an exocyclic, virtually noninteracting double bond. The relative reactivity of the annulene moiety and the C=C double bond in **2** may thus be investigated.

Protonation of **2** with FSO_3H in SO_2ClF at -80 °C in a NMR tube resulted in a red solution of ion **3**. The ^1H and ^{13}C NMR spectra of **3** are displayed in Figure 1, and the chemical shifts, coupling constants, and assignments are given in Table I. Quenching of the ion solution in sodium bicarbonate buffered methanol a -78 °C gives a ca. 60% recovery of **2**, demonstrating that the annulene structure remains intact and that no rearrangement has occurred.

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