molecule in their theoretical treatments of radiationless transitions in molecules. The solvent-dependent quenching of $^1\Delta_g$ oxygen to its ground state is to be contrasted with the somewhat analogous relaxation of triplet state organic molecules which (aside from heavy atom effects) is relatively independent of solvent because large molecules have sufficiently large numbers of internal vibrational modes to act as their own heat sinks.[10]

Even at this preliminary stage of investigation it is clear that certain solvent properties are unimportant in affecting the lifetime of singlet oxygen. The fact that the lifetime is shortest in water might suggest that the dielectric constant or dipole moment of the solvent molecules is an important parameter, but this possibility is eliminated by the fact that the lifetime is almost the same in both benzene and acetone. Comparison of the data in Table I further demonstrates that there is no correlation between viscosity and lifetime. Foote has also arrived at similar conclusions.[2]

Our observation that the lifetime of singlet oxygen is quite sensitive to the nature of the solvent appears to be at variance with conclusions reached by other workers, and it is worthwhile to see how this discrepancy might have arisen. Many of the previous studies of dye-sensitized photooxidation involved mixed solvents, and using the numbers in Table I we compute that the lifetime of $^1\Delta_g$ in a 4:1 mixture of benzene and methanol (a common mixture)[2,6] would be 16 μsec. This is considerably reduced from the lifetime in neat benzene, so it is easy to see that incorporation of small amounts of methanol in varous solvents would prevent observation of large solvent effects on the lifetime of $^1\Delta_g$. Furthermore, reaction rate constants of certain acceptors may be solvent dependent (the rate constant for 1,3-diphenylisobenzofuran in CS_2 is about one-half its value in methanol) and therefore obscure lifetime changes.

We are continuing our investigation of the various factors which influence the lifetime of $^1\Delta_g$ in solution, and a more detailed experimental and theoretical analysis of these observations follows.[14]

(14) P. B. Merkel, R. Nilsson, and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 1030 (1972).

Paul B. Merkel, David R. Kearns*
Department of Chemistry, University of California
Riverside, California 92502
Received October 22, 1971

Deuterium Effects on Singlet Oxygen Lifetimes in Solutions. A New Test of Singlet Oxygen Reactions

Sir:

Work during the past 6 years has clearly established the central role which singlet oxygen plays in a number of dye-sensitized photooxidation reactions of simple organic acceptors.[1-6] On the basis of this work singlet oxygen has also been proposed as the reactive intermediate in a variety of other reactions, including the ozone phosphite oxidations[7,8] and the photooxidation of amines[6,9,10] and amino acids and nucleic acids.[11,12] However, because of a variety of problems (solubility, lack of volatility, possible reaction with excited sensitizers,[13] sensitivity of acceptors to peroxide and radical oxidation)[8,14,15] it has been very difficult to determine whether or not these reactions involve singlet oxygen. In view of these difficulties we felt that it was essential to have additional criteria to determine whether or not an oxidation reaction involves singlet oxygen and which could be used in a wide range of solvents and would not be susceptible to the limitations of the β-carotene[16,17] or azide quenching test.[18] In this communication we report the development of a simple diagnostic test for singlet oxygen reactions which appears to be free of most of these limitations.

The basis of this test follows directly from our recent discovery that the lifetime of singlet oxygen is extremely sensitive to the nature of the solvent[19,20] and that there is a direct correlation between the lifetime of singlet oxygen and the intensity of the infrared absorption of the solvent.[20] This correlation, which has now been confirmed in a number of different solvents, has permitted us to derive the following approximate expression relating the two quantities[20]

$$\frac{1}{\tau}\,(\mu\text{sec}^{-1}) \simeq 0.5(\text{OD}_{1270}) + 0.05(\text{OD}_{1590}) + \cdots$$

where OD_{1270} and OD_{1590} are the optical densities of 1 cm of solvent at 1270 and 1590 nm, respectively, and additional terms may be neglected for most solvents where $\tau \lesssim 40$ μsec. Since much of the solvent absorption intensity in this region is due to OH or CH vibrations (overtones and combinations), it was immediately apparent that there could be large changes in the singlet oxygen lifetime in going from a normal solvent to a perdeuterated solvent. For photosensitized oxidation reactions this carries with it the additional prediction that the "β" value for a given acceptor (the ratio of the rate of decay of singlet oxygen to the reaction rate with singlet oxygen) should show a similar variation, since reaction rate constants are not expected to be altered significantly upon solvent deuteration. In fact, we have shown that for DPBF rate constants do not vary greatly even with large changes in solvent character.[20]

We recently developed a direct method for measuring the lifetime of singlet oxygen and have now used this to examine the effect of solvent deuteration on singlet oxygen lifetimes.[19-21] In these experiments the singlet

(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) C. S. Foote, *Science*, **162**, 963 (1968).
(4) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).
(5) K. Gollnick, *Advan. Chem. Ser.*, No. **77**, 78 (1968).
(6) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).
(7) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **90**, 537 (1968); **90**, 4161 (1968); **91**, 5358 (1969).
(8) P. D. Bartlett and G. D. Mendenhall, *ibid.*, **92**, 210 (1970).
(9) R. F. Bartholomew and R. S. Davidson, *Chem. Commun.*, 1174 (1970).
(10) M. H. Fisch, J. C. Gramain, and J. A. Oleson, *ibid.*, 13 (1970).
(11) J. D. Spikes and R. Livingston, *Advan. Radiat. Res.*, **3**, 29 (1969).
(12) F. R. Hallett, B. P. Hallett, and W. Snipes, *Biophys. J.*, **10**, 305 (1970).
(13) V. Kasche, *ibid.*, **6**, 643 (1967).
(14) R. D. Wayne, *Advan. Photochem.*, **7**, 311 (1969).
(15) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).
(16) C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **90**, 6233 (1968).
(17) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970).
(18) N. Hasty, P. Merkel, P. Radlick, and D. R. Kearns, *Tetrahedron Lett.*, 49 (1972).
(19) P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 1029 (1972).
(20) P. B. Merkel and D. R. Kearns, to be submitted for publication.

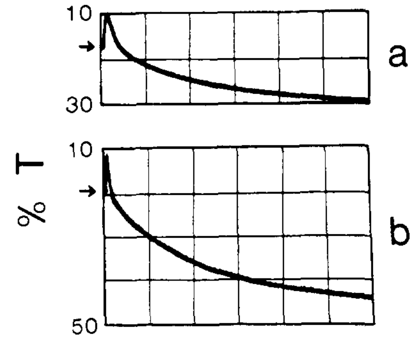

Figure 1. Bleaching in oxygenated solutions of 1,3-diphenylisobenzofuran (1.5×10^{-5} M) monitored at 410 nm in a 1-cm cell: (a) 1:1 H_2O-CH_3OH, 1 div = 2 μsec; (b) 1:1 D_2O-CH_3OH, 1 div = 5 μsec. The concentration of methylene blue was 5×10^{-5} M; arrows indicate % T before pulse.

oxygen was generated in $<5 \times 10^{-7}$ sec by energy transfer from methylene blue triplets produced by a 20-nsec ruby laser pulse. The singlet oxygen was monitored spectroscopically by following its reaction with the colored acceptor, 1,3-diphenylisobenzofuran (DPBF), to form a colorless product. Measurements of bleaching at two acceptor concentrations provide values for both the singlet oxygen lifetime and the reaction rate constant.

When the DPBF is kept sufficiently low such that reaction is not a major decay pathway for $^1\Delta$ the rate of bleaching provides the lifetime of singlet oxygen directly. Bleaching curves obtained under these conditions for 1:1 H_2O-CH_3OH and 1:1 D_2O-CH_3OH solutions are illustrated in Figures 1a and b, respectively. In the former solvent the lifetime is measured to be 3.5 μsec while $OD_{1270} = 0.33$ and $OD_{1590} = 3.7$. In the latter solvent the OD's are reduced by a factor of ~3 ($OD_{1270} = 0.10$ and $OD_{1590} = 1.0$) and, as expected, the singlet oxygen lifetime increases by a factor of 3, to 11 μsec. In 1:1 D_2O-CD_3OD ($OD_{1270} = 0.03$ and $OD_{1590} = 0.3$) the $^1\Delta$ lifetime is predicted to be ~35 μsec.

While we have not yet carried out a direct measurement of the decay of $^1\Delta$ in the 1:1 D_2O-CD_3OD mixture, our prediction has been confirmed by steady state measurements of photoxidation efficiencies. In these experiments we monitored the methylene blue photosensitized bleaching of DPBF (10^{-5} M)[22] in 1:1 H_2O-CH_3OH and 1:1 D_2O-CD_3OD under identical conditions and observed a tenfold increase in efficiency of photooxidation in the deuterated solvent. Since, as we have noted, the reaction rate constant is unaffected by deuteration, a tenfold increase in the lifetime of singlet oxygen is implicated.

The same sort of experiments (reported in more detail elsewhere)[23] were carried out in these solvents for the amino acid tryptophan for which the mechanism of sensitized photooxidation has been uncertain.[11] A similar tenfold increase in bleaching of tryptophan absorption was observed for the deuterated mixed solvent.

We have previously measured a lifetime of 2 μsec for singlet oxygen in water.[19,20] Comparison of the infrared absorption intensities of H_2O and D_2O suggests that the lifetime in the latter solvent should increase by approximately a factor of 9. Again this prediction was checked by comparison of the rates of methylene blue (2×10^{-6} M) photosensitized oxidation of tryptophan (10^{-4} M) in air-saturated H_2O and D_2O. Figure 2 demonstrates that while the rate of bleaching of tryptophan in H_2O is 0.1%/min, the rate in D_2O is 1%/min indicating a $^1\Delta$ lifetime in D_2O of 20 μsec. These observations provide compelling evidence that the photobleaching of tryptophan occurs *via* a singlet oxygen mechanism. From comparison of the photooxidation rates of tryptophan and DPBF we have calculated a rate constant of $k = 4 \times 10^6$ M^{-1} sec^{-1} for reaction between tryptophan and singlet oxygen.

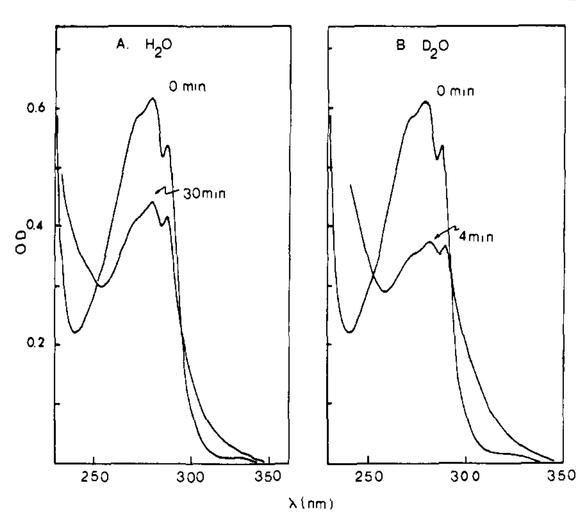

Figure 2. The methylene blue sensitized photobleaching of tryptophan (10^{-4} M) in (a) H_2O and in (b) D_2O in an air-saturated solution containing 2×10^{-6} M methylene blue.

The above studies confirm our theoretical prediction[20] that there should be large deuterium effects on the lifetime of singlet oxygen and provide a totally new method for determining the role of singlet oxygen in oxidation reaction. This method has the great virtue that it does not require addition of foreign components to a solvent (as in the azide or β-carotene quenching) which might react with excited dye or singlet oxygen, nor is there any change in most properties of the solvent.

It is important to note that deuteration will not always lead to an increase in the singlet oxygen lifetime and might in certain instances bring about increased decay rates. For example, a relatively small deuterium effect is expected for acetone and this has been substantiated by preliminary measurements of photooxidation efficiencies. Methanol, on the other hand, appears to be a suitable solvent for characterization of singlet oxygen reactions since an order of magnitude $^1\Delta$ lifetime increase upon deuteration is predicted.

Acknowledgment. R. Nilsson thanks Wallenberg-stiftelson jubileums donation (Sweden) for a travel grant. The support of the U. S. Public Health Service (Grant CA 11459) is most gratefully acknowledged.

Paul B. Merkel, Robert Nilsson, David R. Kearns*
Department of Chemistry, University of California
Riverside, California 92502

Received November 8, 1971

---

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

(22) At this concentration DPBF does not appreciably reduce the $^1\Delta$ lifetime.

(23) R. Nilsson, P. B. Merkel, and D. R. Kearns, *Photochem. Photobiol.*, in press.