The Determination of Rate Constants of Reaction and Lifetimes of Singlet Oxygen in Solution by a Flash Photolysis Technique

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Abstract: A flash photolysis technique, employing a dye-laser as the flash excitation source, was developed to determine, directly, the rate constant of decay (k_d) of singlet oxygen ($O_2{}^1\Delta_g$) and rate constant of reaction (k_{rx}) between singlet oxygen and 1,3-diphenylisobenzofuran, DPBF, in a variety of solvents. Some results are the following: methanol, $k_d = (9.0 \pm 0.6) \times 10^4$ sec^{-1}, $k_{rx} = (1.3 \pm 0.1) \times 10^9$ sec^{-1} M^{-1}, $k_d/k_{rx} = 7.2 \times 10^{-5}$ M; *n*-butyl alcohol, $k_d = (5.2 \pm 0.8) \times 10^4$ sec^{-1}, $k_{rx} = (0.80 \pm 0.2) \times 10^9$ sec^{-1} M^{-1}, $k_d/k_{rx} = 6.5 \times 10^{-6}$ M; *tert*-butyl alcohol, $k_d = (3.0 \pm 0.4) \times 10^4$ sec^{-1}, $k_{rx} = (0.57 \pm 0.08) \times 10^9$ sec^{-1} M^{-1}, $k_d/k_{rx} = 5.3 \times 10^{-5}$ M. Values in benzene:methanol (4:1), bromobenzene:methanol (4:1), pyridine, dioxane, methanol:water (1:1), methanol:glycol (1:1), and glycol were also obtained. The resulting β values (k_d/k_{rx}) are in good agreement with β values determined in other ways. The technique was also shown useful for determination of absolute rate constants of reaction with or quenching of singlet oxygen by compounds such as 2,5-diphenylfuran and *N,N*-dimethylaniline.

Due to the wide interest in and application of singlet oxygen chemistry, it is of importance to know the lifetime of singlet oxygen in various solvents.

Early attempts to determine the lifetime of the reactive intermediate, singlet oxygen, in photooxidation reactions resulted in a lower limit of a few hundred nanoseconds.[1] More recently, several research workers have used β-carotene to quench singlet oxygen, and from the results and with the assumption that the quenching action occurs at the diffusion limit, they have calculated the lifetime of singlet oxygen in various solvents.[2–4] The results are dependent upon the knowledge of the rate constants of diffusion which vary considerably for a given solvent.[5,6]

Although determination of β values (k_d/k_{rx}) for reactions between singlet oxygen and an acceptor suffer from some limitations, the values are becoming more reliable and are now easily obtained.[3] In many cases it is desirable to know the variation of the lifetime of singlet oxygen and its rate constant of reaction as a function of some parameter (*i.e.*, solvent polarity). Variations in these individual rate constants can be hidden if only their ratio is measured. As an example of this limitation, Foote found no relation between β values and the polarity or viscosity of the solvent.[7] On the other hand, Young and coworkers found that there was a relationship between solvent polarity and relative rate constants of reaction for substituted furans and other compounds.[3,4,8] The assumptions inherent in the technique and interference with the excited states of the dye-sensitizers could introduce errors into some of these results.

Merkel and Kearns developed a method for determining the rate constant for the decay of singlet oxygen and the rate constant for the rate of reaction of singlet oxygen with 1,3-diphenylisobenzofuran (DPBF).[9] A modification of this technique was used to determine k_d and k_{rx} in a variety of solvents. In addition, the rate constant for quenching of singlet oxygen by *N,N*-dimethylaniline and the rate constant of reaction of 2,5-diphenylfuran with singlet oxygen were determined.

The modified technique involved the use of an organic dye laser to produce a high concentration of singlet oxygen in less than 1 μsec. The rate of decay of singlet oxygen was measured by monitoring the rate of the reaction of singlet oxygen with 1,3-diphenylisobenzofuran, DPBF. Analysis of the data yielded the rate constant of the reaction of DPBF with singlet oxygen (k_{rx}) and the rate constant of the decay of singlet oxygen (k_d). The following kinetic equations illustrate the technique

$$^1\text{Dye-Sens}_0 \xrightarrow[\text{laser}]{h\nu} {}^1\text{Dye-Sens}_1{}^* \xrightarrow{\text{ISC}} {}^3\text{Dye-Sens}_1{}^* \qquad (1)$$

$$^3\text{Dye-Sens}_1{}^* + {}^3O_2 \longrightarrow {}^1\text{Dye-Sens}_0 + {}^1O_2 \qquad (2)$$

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \qquad (3)$$

$$^1O_2 + \text{DPBF} \xrightarrow{k_{rx}} \text{DPBF–}O_2 \longrightarrow \text{products} \qquad (4)$$

where DPBF is assumed to undergo reaction with $O_2{}^1\Delta$ without quenching of $O_2{}^1\Delta$ by comparison with dimethylfuran[3] and ISC refers to intersystem crossing from the singlet manifold to the triplet manifold.

Steps 1 and 2 are fast with respect to steps 3 and 4. Additional rate constants can be studied by including eq 5 in the kinetic scheme. Intense irradiation is neces-

$$^1O_2 + X \xrightarrow{k_q'} \text{products} \qquad (5)$$

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(1) G. O. Schenck and E. Koch, *Z. Elektrochem.*, **64**, 170 (1960).

(2) C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **90**, 6233 (1968); C. S. Foote, Y. C. Chang, and R. W. Denny, *ibid.*, **92**, 5216, 5218 (1970).

(3) R. H. Young, K. Wehrly, and R. L. Martin, *ibid.*, **93**, 5774 (1971).

(4) R. H. Young, R. Martin, K. Wehrly, and D. Feriozi, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, No. PETR 31.

(5) W. R. Ware, *J. Phys. Chem.*, **66**, 455 (1962).

(6) B. Stevens and B. E. Algar, *ibid.*, **72**, 2582 (1968); L. K. Patterson, G. Porter, and M. R. Topp, *Chem. Phys., Lett.* **7**, 612 (1970).

(7) C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **93**, 5168 (1971).

(8) R. H. Young, N. Chinh, and C. Mallon, *Ann. N. Y. Acad. Sci.*, **171**, 130 (1970); R. H. Young, R. L. Martin, N. Chinh, C. Mallon, and R. H. Kayser, *Can. J. Chem.*, **50**, 932 (1972).

(9) P. B. Merkel and D. R. Kearns, *Chem. Phys. Lett.*, **12**, 120 (1971); P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 1029, 1030 (1972).

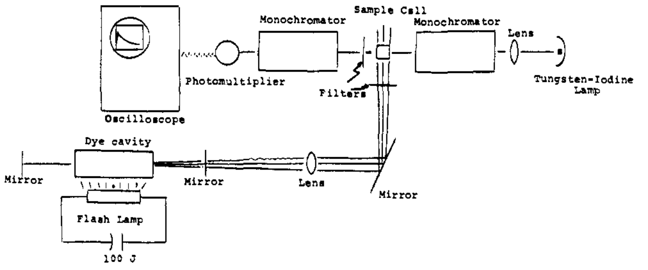

Figure 1. Schematic of the flash photolysis apparatus.

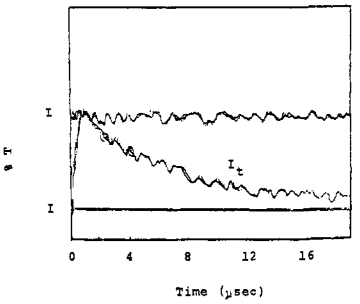

Figure 2. Trace of an oscilloscopic display of the photooxidation reaction of DPBF (I = 34% transmittance (expl 35%)) and (I_∞ = 49% transmittance (exptl 50%)).

sary to induce a detectable depletion in the DPBF concentration. The direct method has the advantage that it permits measurements of interactions between singlet oxygen and organic compounds without any interference from interactions of the dye sensitizer with the organic compound.

Experimental Section

A schematic of the flash photolysis apparatus is given in Figure 1. The reaction mixture was irradiated with a $^1/_4$ J, coaxial dye laser with a flash lifetime of $^1/_2$ μsec and a band pass of 10 nm. The dye used in the laser was either Rhodamine B (610 nm) or Rhodamine 6G (583 nm). The homogeniety of the laser radiation at the reaction cell was checked by observing burn spots on carbon paper and polaroid film. The monochromators were adjusted to pass 410-nm radiation with a band pass of 3.2 nm. Scattered light from the flashlamp was removed by the use of filters and the second monochromator. In many cases a differential preamplifier was used in the oscilloscope to increase the observability of small changes in the intensity of the 410-nm radiation.

The dye sensitizers, Methylene Blue and Rose Bengal, were obtained from Fisher Chemical Co. and used as received. 1,3-Diphenylisobenzofuran was obtained from Aldrich Chemical Co. and was used as received. *N,N*-Dimethylaniline was obtained from Fisher Chemical Co. while 2,5-diphenylfuran was obtained from Dr. A. Trozzolo of Bell Laboratories. Methanol and 1-butanol were spectrograde quality; other solvents were commercial grade and used as received. The experimental procedure involved dissolving Methylene Blue (optical density = 0.55 at 610 nm) or Rose Bengal) optical density = 0.14 at 583 nm) and DPBF (from 10^{-5} to 1.5×10^{-4} M) in 1 ml of solvent and saturating the solution with oxygen. The concentration of DPBF was determined from the optical density of the solution and its extinction coefficient at 410 nm (ϵ 23,500 l. mol^{-1} cm^{-1} in methanol with slight variations for the other solvents).

Analysis of Data

The coupled differential equations describing the reaction scheme outlined in eq 1–4 are

$$-\frac{d[\mathrm{DPBF}]}{dt} = k_{\mathrm{rx}}[\mathrm{DPBF}][{}^1\mathrm{O}_2] \qquad (6)$$

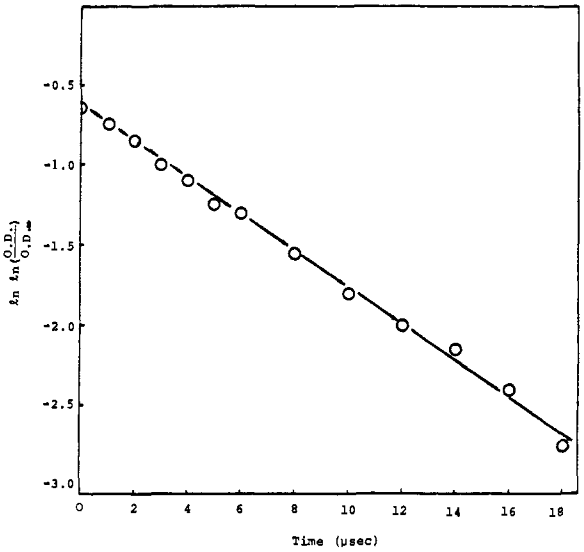

Figure 3. An example of the flash photooxidative decay results of DPBF (data from Figure 2) for the determination of α.

$$-\frac{d[{}^1\mathrm{O}_2]}{dt} = k_{\mathrm{d}}[{}^1\mathrm{O}_2] + k_{\mathrm{rx}}[\mathrm{DPBF}][{}^1\mathrm{O}_2] \qquad (7)$$

An approximate solution (see Appendix A) to these coupled equations is

$$\ln \ln \left[\frac{[\mathrm{DPBF}]_t}{[\mathrm{DPBF}]_{t=\infty}}\right] = \ln \frac{k_{\mathrm{rx}}[{}^1\mathrm{O}_2]_{t=0}}{\alpha} - \alpha t \qquad (8)$$

where

$$\alpha = k_{\mathrm{rx}}[\mathrm{DPBF}] + k_{\mathrm{d}} \qquad (9)$$

Inspection of the above equation shows that the slope of a linear plot of ln ln $[[\mathrm{DPBF}]_t/[\mathrm{DPBF}]_{t=\infty}]$ *vs.* time is equal to α.

The concentration of DPBF was determined from the per cent transmission of 410-nm light. In all cases the initial and final optical densities at 410 nm were checked with an absorption spectrophotometer. Good agreement between optical densities calculated from the oscilloscope trace and spectrophotometer optical densities was obtained. A slight difference in the final optical density was obtained on occasion. This may have been due to the flash area being slightly less than 1 cm^2 or having a slight unevenness in intensity over the cell. The size of the flash area (or unevenness in intensity) did not deviate by more than 20% based on agreement of final calculated and spectrophotometric optical densities. This would result in no more than 5% error in the value of α. No other species present in the solution had significant absorption at this wavelength.

A typical oscilloscope trace is shown in Figure 2. The data obtained from Figure 2 were analyzed and plotted as shown in Figure 3. A value for α was obtained from a straight line drawn through these points. In a similar manner other values of α at various concentrations of 1,3-diphenylisobenzofuran, DPBF, were obtained. A plot of α *vs.* [DPBF] resulted in a line with a slope equal to the rate constant of the reaction between singlet oxygen and DPBF (k_{rx}) and an intercept equal to the rate of decay of singlet oxygen (k_{d}) as shown in Figures 4a and 4b. The concentration of

Table I. Rate Constants of Decay and Reaction of Singlet Oxygen in Various Solvents[a]

Solvent	Dye sensitizer	10^4k_d, sec^{-1}	$10^{-9}k_{rx}$, M^{-1} sec^{-1}	$10^5\beta$, M ($\beta_{lit.}$)[b]	$10^6\tau_0$, sec
Methanol	MB[c]	8.8 ± 0.4	1.3 ± 0.1	6.7 ± 0.3 (7.3 ± 0.7)	11.4 ± 0.6
Methanol	RB[d]	9.7 ± 1.1	1.2 ± 0.4	8.1 ± 1.5 (7.3 ± 0.7)	10 ± 1.0
n-Butyl alcohol	MB	5.2 ± 0.8	0.8 ± 0.2	6.5 ± 1.0 (7.1 ± 0.7)	19 ± 3
tert-Butyl alcohol	MB	3.0 ± 0.4	0.57 ± 0.08	5.3 ± 0.7 (4.9 ± 0.5)	34 ± 4
Benzene:methanol (4:1)	MB	3.8 ± 0.8	0.91 ± 0.2	4.1 ± 0.8	26 ± 5
Bromobenzene:methanol (4:1)	MB	4.3 ± 0.7	0.70 ± 0.13	6.2 ± 1.0	23 ± 4
Pyridine	MB	3.1 ± 1.4	2.1 ± 0.3	1.5 ± 0.7	33 ± 15
Dioxane	MB	2.9 ± 1.0	1.21 ± 0.16	2.4 ± 0.8	32 ± 10

[a] Reported errors are to 95% confidence level. [b] See ref 3. [c] MB refers to Methylene Blue. [d] RB refers to Rose Bengal.

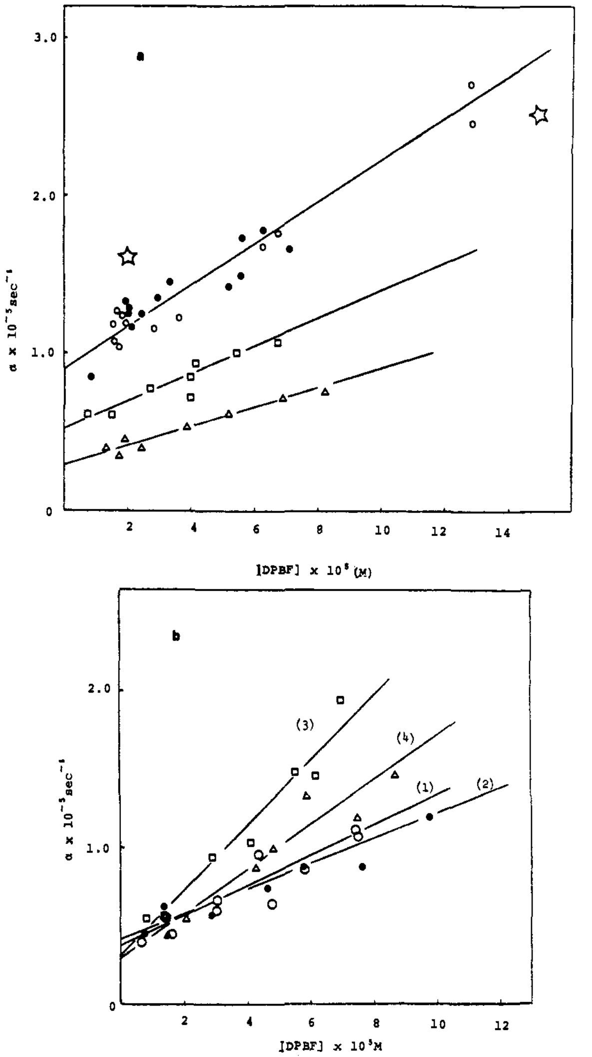

Figure 4 (a). A plot of α *vs.* [DPBF] for the determination of the lifetime of singlet oxygen (and rate constant of reaction) in methanol (○, with Methylene Blue and ● with Rose Bengal), *n*-butyl alcohol (□) and *tert*-butyl alcohol (△) (☆ from ref 9). (b) A plot of α *vs.* [DPBF] for the determination of the lifetime of singlet oxygen (and rate constant of reaction) in (1) benzene:methanol (4:1) (○), (2) bromobenzene:methanol (4:1) (●), (3) dioxane (□), and (4) pyridine (△).

DPBF used in these plots was the average value (see Appendix A).

Another route for singlet oxygen decay results when an additional compound is added to the reaction solution. From a variation of the kinetic equations it can be shown that in this case

$$\alpha = k_{rx}[\mathrm{DPBF}] + k_d + k_q[\mathrm{Q}] \qquad (10)$$

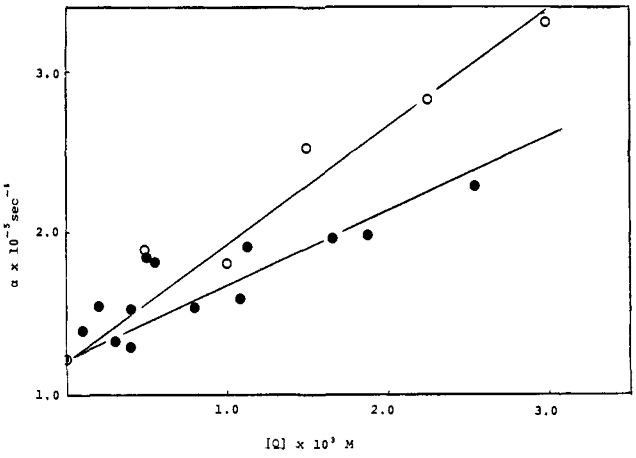

Figure 5. A plot of α *vs.* [Q] for Q = *N*,*N*-dimethylaniline (○) and 2,5-diphenylfuran (●) for the determination of the rate constant of quenching (reaction) of (with) singlet oxygen.

where Q is any compound that intercepts singlet oxygen either by quenching or reaction. At constant [DPBF] a plot of α *vs.* [Q] will give a straight line with a slope equal to the rate constant of quenching or reaction. In this manner the rate constant of quenching, or reaction, of different compounds with singlet oxygen can be determined. This was done for *N*,*N*-dimethylaniline and 2,5-diphenylfuran with Rose Bengal as the dye sensitizer (Figure 5).

Results

The results for the determination of the lifetime of singlet oxygen ($1/k_d$), the rate constant of reaction of singlet oxygen with 1,3-diphenylisobenzofuran, DPBF (k_{rx}), and the resultant β values (k_d/k_{rx}) are given in Tables I and II. The larger percentage error in pyridine and dioxane is the result of the small magnitude of the intercept in these compounds. For compounds with long lifetimes, small errors in the measured points introduce large percentage errors in the intercept.

An estimate of the lifetime can also be obtained by combining β values determined by other methods with a value of α at one concentration of DPBF. Lifetimes calculated by this method are listed in Table II.

Lifetimes of singlet oxygen were measured as a function of the concentration of *N*,*N*-dimethylaniline and 1,3-diphenylfuran. The results of these measurements are summarized in Table III.

Discussion

Lifetimes of Singlet Oxygen in Solution. Lifetimes of singlet oxygen were obtained in several alcohol and

Table II. Rate Constants of Decay of Singlet Oxygen in Various Solvents Determined by an Abbreviated Method[a]

Solvent	$10^5\beta$, M	10^6, sec^{-1}	10^5[DPBF], M	$10^6\tau_0$, sec[b]	$10^{-9}k_{rx}$, sec^{-1} M^{-1}
Methanol:water (1:1)	5.5[c]	3.7 ± 1.2	1.7	3.6 ± 1.2	5.1
Methanol:glycol (1:1)	6.3[d]	1.6 ± 0.1	1.9	8.3 ± 1	1.9
Glycol	31.6[d]	5.1	1.7	2.1	1.5

[a] Reported errors are from average of two measurements. [b] Calculated from ([DPBF] + β)/$\alpha\beta$. [c] Determined from the method described in ref 8. [d] Determined from the method described in ref 3.

Table III. Rate Constants for Quenching/Reaction of Singlet Oxygen by *N,N*-Dimethylaniline and 2,5-Diphenylfuran[a]

Compound	k_{rx}' or k_q, sec^{-1} M^{-1}
N,N-Dimethylaniline	(7.3 ± 0.8) × 10^7
2,5-Diphenylfuran	(4.6 ± 0.78) × 10^7

[a] Reported errors are to a 95% confidence level.

mixed alcohol solvents. In all cases the experimental decay times gave very satisfactory results. Our lifetime measurement in methanol (11.1 ± 0.7 μsec) agrees well with the value obtained by Kearns (7 ± 1 μsec)[9] and Wilkinson (approximately 10 μsec).[10]

In addition, very good agreement was obtained between the β values from the direct method and our previous results as shown in Table I. This is perhaps the best evidence for the reliability of the data. For example, the direct method yielded β values of 7.2 × 10^{-5}, 6.5 × 10^{-5}, and 5.3 × 10^{-5} M for methanol,[11] *n*-butyl alcohol and *tert*-butyl alcohol. These can be compared with the previous results for β of 7.3 × 10^{-5}, 7.1 × 10^{-5}, and 4.9 × 10^{-5} M for the same solvents, respectively.[3]

Solvent Effect on the Lifetime of Singlet Oxygen. Although the lifetimes determined in this paper differ slightly from our results obtained using β-carotene,[3] it is of interest to note that the relative lifetimes are in quite good agreement as can be seen from Table IV.

Table IV. Comparison of the Relative Lifetimes Determined by a Quenching Technique[3] with Those from Table I

Solvent	$\tau_{0_{rel}}$ (from ref 3)	$\tau_{0_{rel}}$ (this work)
Methanol	1.00	1.00
n-Butyl alcohol	1.65	1.79
tert-Butyl alcohol	2.46	3.11
Benzene:methanol (4:1)	1.51 (1.8)[a]	2.45

[a] Calculated from data in paper by E. R. Peterson, K. W. Lee, and C. S. Foote, *J. Amer. Chem. Soc.*, **94**, 1032 (1972).

This means that the solvent effects for the relative rate constants given in the previous work[3,4] are probably quite reasonable and confirms that there are only small solvent effects on the rate constant of reaction of singlet oxygen with most organic compounds.

We had previously suggested that the rate of decay of singlet oxygen in solution is related to the polarity of the solvent.[4] From an analysis of the results of Tables I and II it can be easily seen that there is no relationship with the viscosity of the solvent, and we concur with Kearns and coworkers[9] on this point. However, it does appear that there may be a correlation with the polarity of the solvent. This trend is best seen when comparing alcohol and mixed alcohol solvents. The decrease in lifetime with increasing solvent polarity is not unusual. Fluorescence quantum yields are known to decrease in more polar solvents, perhaps through an "encounter complex" between the solvent and the excited solute.[12] Other factors such as hydrogen bonding should play an important part in such "encounter complexes." For this reason complete comparisons between the solvents considering *only* polarity is somewhat misleading

It is worthwhile noting that there is a negligible heavy-atom effect on the lifetime of singlet oxygen as can be seen by comparing the lifetime in benzene:methanol (4:1), 26 μsec, with bromobenzene:methanol (4:1), 23 μsec. This confirms Foote's previous observation based on relative β values in these solvents.[7]

Rose Bengal *vs.* Methylene Blue. One of the real advantages of the dye laser is the wide range of monochromatic excitation light available from such a flash source. This means that different dye-sensitizers for the photooxidation reactions may be employed which can be a very practical option. For example, the two sensitizers used in this work were excited with different wavelengths: Methylene Blue, 610 nm; Rose Bengal, 583 nm. Good agreement between the lifetimes (11.4 ± 0.6 and 10 ± 1 μsec), rate constants of reaction [(1.3 ± 0.1) × 10^9 and (1.2 ± 0.4) × 10^9 M^{-1} sec^{-1})], and β values [(6.7 ± 0.3) × 10^{-5} and (8.1 ± 1.5) × 10^{-5} M)] were obtained for the two systems with different sensitizers.

The possibility that the species responsible for photooxidation reactions is a complex between oxygen and the dye sensitizer has been discussed by several workers.[13,14] In addition to their evidence, this intermediate can be eliminated because neither the lifetime of the reactive species nor the rate constant of the reaction with DPBF are a function of the dye sensitizer (see Table I). It is unlikely that any form of a sensitizer–O_2 complex would have the same lifetime and rate of reaction with different sensitizers. This confirms that the reactive species is singlet oxygen in dye-sensitized photooxidation reactions.

Conclusions

A new technique for the determination of lifetimes of singlet oxygen in solution and the determination of

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[10] See comment in paper by C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, **171**, 139 (1970).

[11] Results in methanol were determined from a plot of all the α values with both Methylene Blue and Rose Bengal used as sensitizers.

[12] D. M. Hercules, "Fluorescence and Phosphorescence Analysis," Interscience, New York, N. Y., 1966, p 107.

[13] E. J. Corey and W. C. Taylor, *J. Amer. Chem. Soc.*, **86**, 3881 (1964); C. S. Foote and S. Wexler, *ibid.*, **86**, 3879 (1964).

[14] K. Gollnick, T. Franken, G. Schade, and G. Dorhofer, *Ann. N. Y. Acad. Sci.*, **171**, 89 (1970).

absolute rate constants of reaction between singlet oxygen and various organic acceptors was developed. Good agreement between the β values found in this manner and those reported in the literature was obtained emphasizing the reliability of the method. In addition, a variation of the technique enabled the determination of the rate constant of quenching (*N*,*N*-dimethylaniline)[10] and the rate constant of reaction (DPF[15]) of an organic compound with singlet oxygen. This may well be the method of choice for the determination of such rate constants when the interaction between the organic species and the dye sensitizer is unknown. Extensions of the technique for the determination of rate constants of interaction (reaction and/or quenching) will be given elsewhere.

Appendix A

The coupled differential equations describing the decay of $^1O_2$ are listed in the text (eq 6 and 7) and repeated here for clarity.

$$\frac{d[\text{DPBF}]}{dt} = -k_{rx}[^1O_2][\text{DPBF}] \qquad (1A)$$

$$\frac{d[^1O_2]}{dt} = -[k_{rx}[\text{DPBF}] + k_d][^1O_2] \qquad (2A)$$

Let

$$\alpha = k_{rx}[\text{DPBF}] + k_d \qquad (3A)$$

Assume that α is constant. This assumption is essentially true if [DPBF] is small or if the amount of the reaction is small. The error introduced by this assumption will be discussed below. The solution of eq 2A is

$$[^1O_2]_t = [^1O_2]_{t=0}e^{-\alpha t} \qquad (4A)$$

When this solution is substituted into eq 1A the solution of eq 1A is

$$\ln\left[\frac{\text{DPBF}]_t}{[\text{DPBF}]_{t=\infty}}\right] = \frac{k_{rx}[^1O_2]_{t=0}e^{-\alpha t}}{\alpha} \qquad (5A)$$

This equation is equivalent to eq 8 in the main text and was used for the analysis of the data.[16]

In order to evaluate the errors introduced by assuming α is a constant, the coupled equations eq 1A and eq 2A were solved by a Runge–Kutta[17] technique on a computer. When reasonable values of the parameters were used, even when large amounts of DPBF were consumed (as much as 50%), the difference between a "true" α and the α derived from the linear plot described in the text was less than 15%, if the *average* concentration of DPBF was used in the calculation of the "true" α. For example, in methanol the change in DPBF concentration was about 30% at low concentrations (10^{-5} *M*) which results in a 5% change in α. At higher concentrations of DPBF (up to 1.5×10^{-4} *M*) the reaction resulted in about a 10–15% change in [DPBF] or a 10–12% change in the value of α. Use of average concentrations of [DPBF] in these cases reduced the error to less than 10%.

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(15) DPF is assumed to undergo reaction with $O_2{}^1\Delta$ without quenching of $O_2{}^1\Delta$ by comparison with dimethylfuran.[3]

(16) The equation used by Kearns, *et al.*,[9] is essentially equivalent to eq 5A. The additional assumptions used by them introduce no more than 10% error under the conditions used in these experiments.

(17) H. Morgenau and G. M. Murphy, "Mathematics of Physics and Chemistry," Van Nostrand, Princeton, N. J., 1956, p 486.

(18) Note Added in Proof. Two recent publications by Kearns[19] and Wilkinson[20] illustrate variations of the technique presented in this paper. Their results for the lifetime of singlet oxygen ($^1O_2$) in comparable solvents agree reasonably well with our results. Their values for other solvents in addition to ours give a large number of solvent-lifetime results. However, we do advise some caution in the use of these results. The reactivity of the acceptor, DPBF, varies in different solvents. In most cases the reaction of $^1O_2$ with DPBF contributes significantly to the decay rate of $^1O_2$ at the concentrations of DPBF used in the experiments. This leads to low values for the lifetime of $^1O_2$ unless this factor is taken into consideration. Indeed if Wilkinson's values for the lifetime of $^1O_2$ in methanol ($\tau = 6$ μsec) and benzene:methanol (4:1, $\tau = 10$ μsec) are corrected for reaction by DPBF using the β (k_d/k_{rx}) ratios given in this paper, the agreement of the lifetimes with our results is extremely good (corrected results 10.5 μsec (ours 11 μsec) and 23 μsec (ours 26 μsec) for methanol and benzene: methanol, respectively). This makes it imperative that the effect of variation of the concentration of the acceptor (DPBF) be considered carefully. For the solvents which have very long lifetimes this becomes more important. If a solvent has both a small k_d and a large k_{rx} (low β value), then the experimental method used here is not capable of determination of the lifetime with a reasonable degree of accuracy as the intercept of the plot of α *vs.* [DPBF] passes too close to zero. This means that accurate β values should be obtained where possible in order to confirm the potential accuracy of the experimental results for all solvents.

(19) P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, 94, 7244 (1972).

(20) D. R. Adams and F. Wilkinson, *J. Chem. Soc.*, *Faraday Trans.*, 586 (1972).