Solvent Effects in Dye-Sensitized Photooxidation Reactions

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Abstract: The problem of interpretation of solvent effects in photooxidation reactions has been due to the inability of researchers to distinguish between solvent effects on the rates of decay of singlet oxygen and the rate constants for the reactions of singlet oxygen with organic compounds. Up to this time only a ratio of these values (β value) was experimentally possible to obtain. This causes confusion as to whether differing solvents change the rate of decay, the rate constant for the reaction, or both. We have recently shown a relation between solvent polarity and Hammett ρ values for a series of solvents. This evidence suggests that there is a relationship between the rate constant for the reaction of organic compounds with singlet oxygen and the polarity of the solvent used. In an effort to clarify the situation we have developed a new method to determine β values (k_d/k_{rx}) and have adapted this to calculate the β value of a very reactive species, β-carotene (β in the order of 3–6 $\times$ 10^{-6} depending upon the solvent). Assuming that the rate of reaction (k_{rx}), or the rate of quenching of singlet oxygen by the β-carotene, is diffusion controlled, we have been able to obtain absolute rates of decay (k_d) of singlet oxygen in different solvents. If the β value (k_d/k_{rx}) is known for the reaction of a specific compound with singlet oxygen in a solvent where the rate of decay of the excited singlet oxygen species has been determined, then the absolute rate constant for the reaction can be calculated.

Solvent effects in photooxidation reactions have puzzled us and other researchers for some time. Foote has written that for the photooxidation of 2-methyl-2-pentane in a series of solvents that "no trend in the results (β values) with polarity is observed..." and "further no effect of viscosity is observed...."[2] Gollnick in his excellent review of photooxidation reactions more than once refers to the confusing effect of solvents on photooxidation reactions and the lifetimes of singlet oxygen in various solvents.[3] The reason in both cases is that the only measure of reactivity of organic compounds with singlet oxygen is the measurement of β values (rate of decay/rate of reaction or k_d/k_{rx}). The solvent may affect either or both the rate of reaction (k_{rx}) and the rate of decay of the singlet oxygen (k_d).

We have previously indicated that there does seem to be a regular solvent effect on the rate of photooxidation reactions as determined by changing Hammett ρ values in a series of solvents.[4] A good correlation was obtained for a plot of $1/\epsilon$ (ϵ is the dielectric constant for each solvent) *vs.* these Hammett ρ values.

To our knowledge this was the first case in which some solvent parameter was correlated with photooxidation reactions. However, the relative β values were not consistent with the polarity of the solvents. It appeared that the value of the $1/\beta$ (rel) was anomalous in glycol solvent. The reason may be that the rate of decay of singlet oxygen in the more viscous glycol solution was changed substantially from that of other solvents.

For these reasons we have expanded our studies on the effect of solvents on the decay rate of singlet oxygen and the rate constants for dye-sensitized photooxidation reactions.
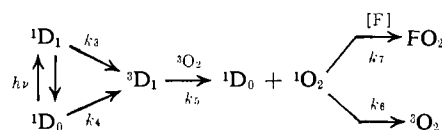
Results and Discussion

The most currently acceptable scheme for dye-sensitized photooxidation reactions is outlined here

where D represents the dye-sensitizer (in our case rose bengal) and F represents any organic compound which reacts with singlet oxygen ($^1\Delta$, $^1O_2$).

The quantum yield for the disappearence of the organic species is given by

$$\Phi_{-F} = K\frac{k_7[F]}{k_7[F] + k_6}$$

or

$$\Phi_{-F} = K\frac{[F]}{[F] + \beta}$$

where

$$\beta = \frac{k_6}{k_7}$$

Usually this β value of the photooxidation reaction is determined by plotting $1/\Phi_{-F}$ *vs.* $1/[F]$ when the values of [F] and β are comparable.[2] The errors in this method have been estimated to be $\pm 30\%$.[2] Other methods also have been used.[5]

These β values in essence are an index of reactivity of particular organic compounds with singlet oxygen and as such are important in such fields as air pollution, oxidations of biologically related compounds, etc. For these reasons we have had an interest in developing other methods of measuring the reactivity of such organic compounds with singlet oxygen, especially for compounds where the standard methods are not applicable or accurate..

Method for Determination of β Values. Our method involves a quenching of the oxidation reaction of a standard compound (1,3-diphenylisobenzofuran (F)) by the organic compound for which a β value is to be

(1) Holder of an NDEA Fellowship, 1969–1971.
(2) C. S. Foote, *Accounts Chem. Res.*, 1, 104 (1968).
(3) K. Gollnick, *Advan. Photochem.*, 6, 1 (1968).
(4) R. H. Young, N. Chinh, and C. Mallon, *Ann. N. Y. Acad. Sci.*, 171, 130 (1970).

(5) R. Higgins, C. S. Foote, and H. Cheng, *Advan. Chem. Ser.*, No. 77, 102 (1968).

Table I. β Values Obtained in the Photooxidation of Standard Compounds

Compound (X)	Exptl[a] β value	Solvent	Lit.[b] β value
Tetramethylethylene	0.0023	MeOH-*tert*-BuOH (50:50)	0.0027[c]
2-Methyl-2-pentene	0.15	MeOH	0.17[c]
			0.13[d]
	0.12	MeOH-*tert*-BuOH (50:50)	0.14[c]
	0.08	*tert*-BuOH	0.051[c]
cis-4-Methyl-2-pentene	8.0	MeOH-*tert*-BuOH (50:50)	10[c]
2,5-Dimethylfuran	0.00016	MeOH-*tert*-BuOH (50:50)	0.001[c]
	0.00028	MeOH	~0.0002[d]
2-Methylfuran	0.0011	MeOH	~0.0038[d]
2,5-Diphenylfuran	0.00095	MeOH	

[a] Slopes were calculated by a linear regression analysis with a least-squares fit. Errors in the β values from the Stern–Volmer slopes were calculated to be 5–10%. Reproducibility of β values is within the indicated error limits. [b] Errors ±30% or larger. [c] See ref 2. [d] See E. Koch, *Tetrahedron*, **29**, 6295 (1968).

measured. A slight variation of the previous kinetic scheme gives
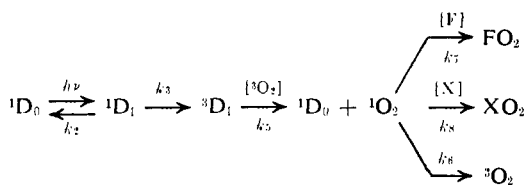
where X is any reactive organic compound. The kinetics of this scheme would be

$$-\frac{d[F]}{dt} = K_{[^1O_2]}\left(\frac{k_7[F]}{k_7[F] + k_8[X] + k_6}\right)$$

where $K_{[^1O_2]}$ would be a constant provided the light intensity, dye concentration, etc., are constant for all reactions. $K_{[^1O_2]}$ is the rate of formation of singlet oxygen.

We use a very low concentration of [F] (about 10^{-6} M) in order to get simplified first-order kinetics. Thus

$$-\frac{d[F]}{dt} = K_{[^1O_2]}\left(\frac{k_7[F]}{k_8[X] + k_6}\right)$$
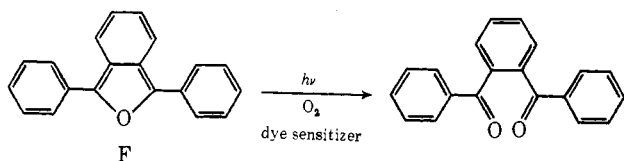
where the slope of the first-order plots will be

$$S = K_{[^1O_2]}\left(\frac{k_7}{k_8[X] + k_6}\right)$$

A typical Stern–Volmer relationship results in

$$S_0/S_x = 1 + (k_8/k_6)[X]$$

and a Stern–Volmer plot of S_0/S_x vs. [X] results in a slope of $k_8/k_6 = 1/\beta$.

The standard compound, F, used was 1,3-diphenyl-isobenzofuran

and the organic compounds used to check the method were tetramethylethylene, 2,5-dimethylfuran, 2-methyl-2-pentene, and *cis*-4-methyl-2-pentene. It should be noted that in order for this method to work a substantial fraction of the 1,3-diphenylisobenzofuran, F, must react with little change in the concentration of compound X. This can be easily confirmed by obtaining linear first-order plots. The standard com-

pound, F, is one of the most reactive with singlet oxygen, with a reported β value of about 10^{-4}. Thus it is ideal for such measurements. The method involves following the disappearance of F by measuring changes in the fluorescence intensity at λ_{max} (excitation 405 nm, emission 458 nm).

Good first-order plots were obtained and the relative slopes used directly in the Stern–Volmer relationship to obtain β values. The β values for a series of compounds are reported in Table I.

The value for dimethylfuran (DMF) (2×10^{-4}) is lower than that reported by Foote[2] (1×10^{-3}). However, Koch[6] reported a value of 2×10^{-4} and the ratio of rate constants of reaction of singlet oxygen with tetramethylethylene (TME)–dimethylfuran (DMF) obtained by Ogryzlo[7] was 1:3.4, by Herron[8] was 1:17, and by Timmons[9] was 1:6 all for gas-phase results, compared to our solution ratio of 1:12–15. Certainly the ratio of these rate constants does vary considerably. It should be noted that DMF is not pure when obtained commercially and it does decompose and should be purified immediately prior to use in order to get good results.

It is conceivable that as we are really measuring the ability of these compounds to quench singlet oxygen and we are assuming that this is *via* reaction, we may be observing some quenching other than reaction quenching. This appears to be unlikely as Timmons reports that the chemical reactions of TME and DMF are much greater than any collisional deactivation process.[9]

The other β values of the photooxidation reactions of singlet oxygen with the various alkenes show excellent correlation with those reported in the literature; thus we feel the method is reasonably reliable and efficient. The method is somewhat similar to that used by Wilson.[10] However, in her case only relative β values could be obtained from the quenching reactions, much like the results of Foote and others.[2,5] In our case, due to the unique conditions of low concentration of reactant (1,3-diphenylisobenzofuran, $\approx 10^{-6}$ M) and method of analysis (fluorescence), we were able to obtain absolute β values directly from the slope of the

(6) See Table I, footnote *d*.

(7) K. Furukawa, E. W. Gray, and E. A. Ogryzlo, *Ann. N. Y. Acad. Sci.*, **171**, 175 (1970).

(8) J. T. Herron and R. E. Huie, *ibid.*, **171**, 229 (1970); *J. Chem. Phys.*, **51**, 4164 (1969).

(9) G. A. Hollinder and R. B. Timmons, *J. Amer. Chem. Soc.*, **92**, 4181 (1970).

(10) T. Wilson *ibid.*, **88**, 2898 (1966).

Stern–Volmer quenching plots. It would appear that if there is no interference in the absorption or fluorescence regions of the standard compound that it can be used to give accurate β values in a minimum of time. It probably is not applicable to some of the polynuclear aromatic compounds. However, these can be related rather easily and accurately to known compounds.[4]

Solvent Effect on Decay Rates of Singlet Oxygen ($^1\Delta_g$). Our initial studies to explore the effects of solvents on the lifetime of singlet oxygen involved the use of a solvent pair (methanol–glycol). Because of the similarity of their dielectrics (methanol 32.6 and glycol 37.7) this solvent system should show the effects of viscosity only. We used solutions of 1,3-diphenyl-isobenzofuran at low concentrations and obtained relative β values by our normal technique. An absolute β value was determined by the method described in the previous section for methanol solvent only.

Viscosities of solvents were calculated by the normal method at 28°.[11] The viscosity values and relative β values obtained are given in Table II.

Table II. Solvent Effects on the β Value of 2,5-Diphenylfuran

Solvent Methanol–glycol, $\%^a$	Viscosity^b	$1/\beta(\text{rel})^{c-f}$
100	0.538	1.00
75	1.15	1.73
50	2.42	2.82
25	6.17	3.60
0	15.6	2.73

^{a} Volume per cent methanol. ^{b} Viscosity measurements at 28° using an adaptation of an Ostwald type viscometer. ^{c} No cut-off or interference filter used, rose bengal used as the dye sensitizer. ^{d} Values for $1/\beta(\text{rel})$ were calculated from the absolute β value of 2,5-diphenylfuran in methanol (see ref 4 for method). ^{e} Obtained from relative first-order plots using a low concentration of the diphenylfuran, followed by changes in fluorescence intensity (excitation 311 nm, emission 374 nm). ^{f} Includes small correction for changes in absorption of light by the rose bengal.

It can be seen from Table II that there is a regular decrease in β values, as expected for a decrease in the rate of decay of singlet oxygen with increasing viscosity of solvents. The slight anomalous result for 100% glycol could be due to either an effect on the β value through a significant change in the rate of reaction (k_{rx}) caused by polarity effects or to a specific solvent effect on either k_d or k_{rx} by the glycol.

In an effort to increase the understanding of these results further studies were carried out. A variation of the new method described above was used to obtain β values for a very "reactive" species, β-carotene. It has been suggested that β-carotene quenches singlet oxygen without chemical reaction; i.e., the reactivity with singlet oxygen is due to quenching only.[12,13]

Previously we said that using this method for determination of β values the standard must react faster (have a lower β value) than the compound being mea-

sured; i.e., 1,3-diphenylisobenzofuran is the best choice. However, as β-carotene quenches without reaction, this requirement is no longer necessary. Our choice of 2,5-diphenylfuran as the new standard reagent was based on the necessity of having a compound whose excitation and emission wavelengths are not obscured by the absorption of β-carotene. 2,5-Diphenylfuran is a good choice for this reason.[14]

The β value obtained for β-carotene from the slope of the Stern–Volmer quenching plot is equal to the rate of decay (k_6 or k_d) divided by the rate of quenching (k_8 or k_q) of the singlet oxygen by the carotene.

$$1/\text{slope} = \beta = k_d/k_8$$

Foote has previously used β-carotene to obtain an approximate decay rate for singlet oxygen in benzene–methanol (4:1).[12] He also suggested that the rate of quenching by β-carotene could be diffusion controlled.[13] His elaborate method, however, resulted in rather large errors in the results. We feel our method is experimentally easier, quicker, and more versatile.

If the rate of quenching of singlet oxygen by β-carotene is diffusion controlled then the rate constant for diffusion in the solvents we wish to use is necessary. As the Stokes–Einstein equation has been shown to be in error when one of the diffusing species is small, we used the data reported by Ware to obtain approximate rates of diffusion.[15] Ware obtained the rates of diffusion of oxygen in various solvents (including a number of alcohols of varying viscosity) via quenching of fluorescence of some aromatic molecules. These rates were later shown to be quite good by other workers.[16] All other factors being equal (solvent interactions with the diffusing molecules as well as size) it is probable that the rate of diffusion of singlet oxygen may well be the same as ground-state oxygen. If this is true then Ware's data can be used to obtain rates of diffusion of singlet oxygen and hence rates of decay from the β value of the quenching process of singlet oxygen by β-carotene.

Although methanol was the only solvent we used in which the rate of diffusion of oxygen had been measured, Ware did find a qualitative correlation between the reciprocal viscosity values for a series of solvents (11) and the rate of oxygen diffusion. Assuming a straight line for the viscosity range used ($k_d = 1.81 \times 10^{10} + 0.638 \times 10^{10} \times \eta^{-1}$; $r = 0.93$) we obtained estimated rates of diffusion of oxygen in our solvents and these are recorded in Table III.

Although there are problems with the determination of rate constants for diffusion-controlled reactions[17] these diffusion rates used for singlet oxygen are probably the best possible at this time.[18]

Also given in Table III are the β values (k_d/k_q) for β-carotene and the calculated rate of decay assuming diffusion rate control for the rates of quenching of singlet oxygen.

(11) A. C. Merrington, "Viscometry," Edward Arnold & Co., London, 1949, p 20.
(12) C. S. Foote and R. W. Denny, J. Amer. Chem. Soc., 90, 6233 (1968).
(13) C. S. Foote, Y. C. Chang, and R. W. Denny, ibid., 92, 5216, 5218 (1970).
(14) We have recently been using rubene (filters must be used) with methylene blue to obtain similar results: R. H. Young and D. Feriozi, unpublished research, Georgetown University.
(15) W. R. Ware, J. Phys. Chem., 66, 455 (1962).
(16) (a) B. Stevens and B. E. Algar, ibid., 72, 2582 (1968); (b) L. K. Patterson, G. Porter, and M. R. Topp, Chem. Phys., Lett., 7, 612 (1970).
(17) P. J. Wagner, Symposium on the Frontiers in Photochemistry, New York, N. Y., Oct 1970.
(18) We wish to thank one of the referees for pointing out Ware's results to us.

Table III. Lifetimes of Singlet Oxygen in Various Solvents

Solvent	k_q (rate of diffusion)[a] $\times 10^{-10}$	$1/\eta$ (viscosity) (cP, 25°)	$\beta(k_d/k_q)^b \times 10^6$	$k_d \times 10^{-4}$	τ, sec, $^1O_2$
Methanol[c]	2.98	1.83[d]	6.1	18	0.55 × 10⁻⁵
n-Butyl alcohol	2.06	0.385[d]	5.5	11	0.91 × 10⁻⁵
tert-Butyl alcohol	1.95	0.226[f]	3.8	7.4	1.35 × 10⁻⁵
Benzene–methanol (4:1)	2.94	1.78[e]	3.9	12	0.83 × 10⁻⁵

[a] From our calculations based on Ware's results, ref 15. [b] No autoxidation reactions were observed. [c] Corrected for slight sensitization of the reaction by the β-carotene. Corrections were made for each reaction for each concentration of the carotene used. This was a very small correction. [d] "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p F33. Sometimes interpolated for the temperature given. [e] Determined in our laboratories. [f] J. Timmermanns, "Physico-Chemical Constants of Binary Systems in Concentrated Solutions," Vol. 4, Interscience, New York, N. Y., 1960, p 236.

There are a number of interesting facts which are evident from the results given in Table III. It can be seen that the rate of decay (or the lifetime of singlet oxygen, $^1\Delta_g$) is related to the viscosity of the solvent from methanol (0.547 cP) to tert-butyl alcohol (4.43 cP). The increased stabilization of the excited singlet state of oxygen in the more viscous solvent is quite reasonable and perhaps expected. These may be compared to changes in triplet state lifetimes of organic compounds. This also correlates well with the direction of the effect we obtained from the use of methanol–glycol solvent pairs.

It can also be seen from Table III that the lifetime of singlet oxygen in benzene–methanol of 0.8 × 10⁻⁵ compares favorably with that reported by Foote of approximately 1 × 10⁻⁵ for the same solvent.[19]

Our value differs substantially from that obtained by Koch in methanol for K_d (5 × 10⁶ sec⁻¹).[6]

One of the intriguing factors in the results is the increased lifetime of singlet oxygen in the benzene–methanol solution over that of pure methanol, although they both have almost the same viscosity. Explanations include differences in rate of diffusion from that calculated due to a specific interaction of singlet oxygen with the solvent which does not occur with ground-state oxygen, a deactivating effect of a hydroxyl group, or perhaps the phenyl ring stabilizes singlet oxygen by formation of a weak excimer. Recent preliminary results indicate that it may also be due to a larger decay rate in the more polar solvent.[20]

We have shown that there is a change in the lifetime of singlet oxygen, $^1\Delta_g$, in different solvents and that this change is related to the viscosity of the solvent. The difference in the rate constant for decay in various solvents is sufficiently large to explain the problems in obtaining meaningful results from solvent effects on β values (k_d/k_{rx}). Knowing the absolute rate of decay of singlet oxygen in any specific solvent it is now possible to obtain absolute rate constants for reactions of singlet oxygen with organic compounds in photooxidation reactions. This was done for a series of compounds.

Solvent Effects on the Rate Constant for Dye-Sensitized Photooxidation Reactions. Absolute β values for some compounds were obtained by the method outlined above. Relative β values were found experimentally by the method outlined in a previous publication.[4] Two methods were employed. Limited

information was gained by the use of an appropriate solvent pair, methanol–water. This solvent pair was originally chosen because both solvents have about the same viscosity. If this were the only factor affecting the rate of decay of singlet oxygen then the relative β values should reflect only the change in the rate constant for the reaction due to changes in the polarity of the solvent. The results are given in Table IV.

Table IV. Effects of Solvent Polarity on the Photooxidation of 2,5-Diphenylfuran

Methanol in water[a]	$1/\beta^c$ (rel)	Dielectric $(\epsilon)^b$
100	1.00	32.6
81.37	1.24	36.8
65.79	1.61	41.6
39.79	2.24	53.1
11.5	2.28	69.9
0	2.08	78.5

[a] Mole per cent methanol. [b] Values from J. Timmerman, "Physico-Chemical Constants of Binary Systems in Concentrated Solutions," Vol. 4, Interscience, New York, N. Y., 1960, p 236. [c] β value for the 2,5-diphenylfuran in 100% methane was found to be 9.53 × 10⁻⁴. The others were obtained from relative pseudo-first-order rate constants compared to this value. See ref 4 for method.

A linear correlation between log $1/\beta$(rel) values and $1/\epsilon$ for the photooxidation of 2,5-diphenylfuran in methanol–water was obtained. A specific solvent effect on either k_1 or k_d may be causing a slight problem at high water concentrations.

In our effort to further explore the solvent effects on the rate constant for photooxidation reactions, β values for a series of furans in a series of solvents were obtained. Knowing the rates of decay of singlet oxygen for these solvents it was possible to obtain absolute rate constants. The results are recorded in Table V.

A number of interesting observations can be made from the results recorded in Table II. There is an excellent relationship between increasing polarity of solvent and increasing rates of reaction for all compounds. Also, as expected, the faster the rate of reaction (the larger the rate constant) of the organic species with singlet oxygen, the smaller is the solvent effect. The solvent effect changes from a relatively small ratio of 1:1.7 for the 1,3-diphenylisobenzofuran to 1:32 for the p-chlorophenylfuran (tert-butyl alcohol–methanol).

A good correlation between log k_{rx}(rel) in tert-butyl alcohol, n-butyl alcohol, and methanol and the relative rates in methanol–water mixtures vs. $1/\epsilon$ for all these solvents was obtained for 2,5-diphenylfuran. This gives a polarity range of the solvents from a dielectric

(19) C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, Ann. N. Y. Acad. Sci., 171, 139 (1970).

(20) R. H. Young, R. L. Martin, K. Wehrly, and D. Feriozi, Amer. Chem. Soc., Div. Petrol. Chem., Prepr., 16, A89 (1971); presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

Table V. β Values, Rate Constants, and Relative Rate Constants for a Series of Compounds in a Series of Solvents

Compound	β values $\times 10^4 (k_d/k_{rx}, 25°)$			$k_{rx} \times 10^{-8}$ [a]			k_{rx} (rel)[b,c]		
	MeOH	n-BuOH	tert-BuOH	MeOH	n-BuOH	tert-BuOH	MeOH	n-BuOH	tert-BuOH
2-(p-Chloro-phenyl)furan	27	34	350	0.67	0.32	0.021	32	15	1.00
2-Phenylfuran	17	20	34	1.1	0.55	0.22	5.0	2.5	1.00
2,5-Diphenylfuran	(9.5)[d,e]	9.8	8.0	1.9	1.1	0.93	2.0	1.2	1.00
1,3-Diphenyliso-benzofuran	0.73	0.71	0.49	25	15	15	1.7	1.0	1.00
2-Methyl-2-pentene[e]	1500		810	0.012		0.091	1.3		1.00
Tetramethyl-ethylene[e,f]	46	44	29	0.39	0.25	0.25	1.6	1.0	1.00
2-Methylfuran[e,f]	11	12	6.9	1.6	0.92	1.1	1.5	0.84	1.00

[a] $k_{rx} = k_d/\beta$; k_d (25°) in methanol = 18 × 10⁴; n-butyl alcohol = 11 × 10⁴; tert-butyl alcohol = 7.4 × 10⁴ sec⁻¹. [b] Each set relative to its own rate constant in tert-butyl alcohol. [c] Dielectric of methanol = 32.6; n-butyl alcohol = 17.8; tert-butyl alcohol = 10.9. [d] Determined as an absolute β value. Others for furans are relative to this value as a standard. [e] β value determined by our standard method. [f] Carried out at 23° using a different apparatus, but same method as for e.

of 10 to 80. These results agree with that expected from our previous results where we obtained a correlation between Hammett ρ values and $1/\epsilon$ for a series of solvents.[4]

For the arylfurans there does appear to be a substantial solvent effect which is related to the rate constants for their reactions with singlet oxygen. However, for the "ene" reactions there is very little if any solvent effect regardless of the rates of their reaction. The same is true for one of the simple furans, 2-methylfuran. It is conceivable that the aryl group as a substituent is affecting the symmetry of the approach of the singlet oxygen moiety either by steric interaction or more probably by electronic effects. There continues to be published evidence for concerted Diels–Alder reactions.[21] However, there is some recent work which indicates that in some cases there may be an asymmetric approach of the dienophile on the diene.[22] This would be consistent with our findings on the reactions of furans with singlet oxygen.

Conclusion

A new method for the determination of β values for dye-sensitized photooxidation reactions was developed and confirmed experimentally. This method was applied to determine β values for β-carotene which has been proposed to react (by quenching) with singlet oxygen at the diffusion rate. Making this assumption we obtained absolute rate constants for the decay of singlet oxygen in a variety of solvents. Absolute rate constants for reaction of organic compounds with singlet oxygen can then be calculated with a knowledge of their decay rates and experimental β values.

Experimental Section

Materials. All chemicals were checked for purity by either melting points or glpc prior to use. In most cases the solvents were used directly and where possible spectrograde solvents were used. All solvents were checked for interference of absorption and/or fluorescence and found to be adequate.

Diphenylfuran was obtained from Dr. A. Trozolo of Bell Laboratories which we acknowledge with thanks. The 2-(p-chlorophenyl)furan and the 2-phenylfuran were prepared by the method used by Ayres.[23]

(21) R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, **92**, 4149 (1970).
(22) (a) Y. Kobuke, T. Fueno, and J. Furukawa, *ibid.*, **92**, 6548 (1970); (b) M. J. S. Dewar and R. S. Pyron, *ibid.*, **92**, 3099 (1970).
(23) D. C. Ayres and J. R. Smith, *Chem. Commun.*, 886 (1967); D. C. Ayres, private communications.

Kinetic Studies. Kinetic studies were carried out with a SPF-125 spectrophotofluorometer and a Sargent log linear recorder for direct recording of the first-order plots. The experimental conditions for any reaction series were kept constant, that is, the same light intensity, the same concentration of the dye sensitizer (rose bengal) in the same reaction apparatus. A GE 100-W tungsten lamp was used and the light reflected directly into the constant temperature cuvette chamber of the spectrophotofluorometer at right angles to the excitation and emission light paths. The light was absorbed through 1 cm of solution and was less than 50% absorbed in order to minimize mixing problems. In all cases standard reactions were carried out and these indicated no dark, reversible, or autoxidation occurring.

Determination of β Values. One-milliliter solutions of 10^{-6} M 1,3-diphenylisobenzofuran (DPBF) were placed in a 1-cm spectrofluorometric cell. Five microliters of a 0.72 mg/ml methanol solution of rose bengal was added. The rate of disappearance of the DPBF was followed by monitoring the decrease in fluorescence intensity of the DPBF throughout the course of the photooxidation reaction (excitation, 405 nm; emission, 458 nm). Irradiation for the photooxidation was with a Tungsten lamp and a cut-off filter was used which passed only light above 550 nm. In order to determine the β values, various concentration of each compound were added to the DPBF–rose bengal solutions. It was found that the best results were obtained when these compounds were added in a concentration such that the photooxidation of the DPBF was quenched by no more than 75%. Good first-order plots were obtained for all reactions. It is important that the concentration of the compound whose β value is being measured does not change much throughout the course of the photooxidation of the DPBF. If such a change in concentration occurred, the kinetic results would be invalid. Curvature in first-order plots would be suggestive of a change in the quencher concentration. However, straight lines were obtained in all cases due to the extreme reactivity of the standard, DPBF.

Stern–Volmer quenching plots were obtained for each compound in each solvent. An inverse of the slope of these plots gave the β value directly. The results are recorded in Table I. The β values for the standard compounds, tetramethylethylene and 2,5-dimethylfuran, were reproducible within the error limits reported as determined by experiments carried out independently by two different workers. The Stern–Volmer slopes were calculated by linear regression analysis with a least-squares fit. Errors in the β values were calculated to be 5–10% as determined from the error in the slope of the line.

Use of Solvent Pairs to Study Solvent Effects in Photooxidation Reactions. A. Methanol–Glycol (Viscosity Effects). Methanol–ethylene glycol solution mixtures with 100, 75, 50, 25, and 0% methanol by volume were used. Viscosity measurements at 28° were determined by using an adaption of an Ostwald type viscometer. They were determined by using the formula

$$\eta' = \frac{\eta \rho' t^1}{\rho t}$$

where η' is the viscosity of the unknown liquid; η the viscosity of the standard (methanol); ρ', ρ and t', t are the density and flow time for the unknown and methanol. The results are recorded in Table II.

Diphenylfuran (DPF) was used as a standard. A 10^{-4} M (10 μl) solution of DPF in methanol and 5 μl of a 0.72 mg/ml solution of rose bengal in methanol were added to 1.0 ml of each of the solvent mixtures. No light filter was used in the apparatus and the disappearance of the DPF was followed by a decrease in the fluorescence intensity (excitation, 311 nm; emission, 374 nm).

Corrections for changes in the rate of singlet oxygen produced due to solvent changes in the absorption of light by the rose bengal sensitizer were determined by measurement of the amount of light transmitted through the reaction solution in the region of rose bengal absorption. This was integrated over the absorption wavelength for the dye. Changes in fluorescence of the rose bengal due to solvent changes were experimentally determined to have little effect on the rate of reaction.

Relative rates of the dye-sensitized photooxidation of the diphenylfuran in different solvent mixtures, corrected for changes in the light absorption by the sensitizer, are recorded in Table II.

B. Methanol–Water (Polarity Effects). A series of methanol–water solvent mixtures was prepared as indicated in Table IV. The same procedure as above was used and corrections for changes in the absorption of light by the rose bengal were made although they were small. The corrected relative rates and dielectric constants for each solvent mixture are recorded as well.

Solvent Effects on the Rate of Singlet Oxygen Decay. Quenching of the photooxidation reaction of diphenylfuran (DPF) by β-carotene was carried out to determine β values of the quencher in different solvents. Fresh (benzene) solutions of carotene at 10^{-3} and 10^{-4} M were prepared daily. From 0 to 20 μl of these solutions was added to 10^{-6} M diphenylfuran and 2 μl of the previously mentioned rose bengal solution in 1 ml of some organic solvent. The final carotene concentrations were irradiated through an orange cut-off filter (550 nm) or a Wratten 8 filter (470 nm) depending upon the reaction series. Since carotene absorbs slightly in the region of the filter cut-offs it was necessary to check each solvent at each concentration of carotene for possible sensitization. Slight corrections were necessary only in methanol. Decrease in the fluorescence intensity of the DPF as before was followed at 311-nm excitation and 374-nm emission. In the pure aromatic solvents the rose bengal solubility was questionable. For this reason 20% by volume of methanol in benzene was used. Various concentrations of β-carotene were used to quench the photooxidation reaction of singlet oxygen with the DPF. The relative slopes of good first-order rate plots were used to obtain Stern–Volmer

quenching plots. The slope of these Stern–Volmer plots gave $1/\beta$ values. In all cases at least five points were obtained. The values of β obtained in this manner are recorded in Table III. Errors are in the order of 10% or less as determined by a least-squares fit of the Stern–Volmer plot.

In the solvents used aggregation of the carotene probably did not occur as shown by a linear Beer's plot over the concentrations of β-carotene used.

Solvent Effects on the Rate Constant for Reaction of Singlet Oxygen with an Organic Compound. The rate of photooxidation reactions at low concentrations is given by the following equation

$$\frac{d[x]}{dt} = K_{^1O_2}\frac{k_{rx}[X]}{k_d}$$

where $K_{^1O_2}$ is the rate of formation of singlet oxygen, and k_{rx} is the rate constant for the decay of singlet oxygen. As $k_d/k_{rx} = \beta$-(rel), β values can be obtained for different compounds from the slope of first-order plots if $K_{^1O_2}$ remains constant. This technique was used to obtain relative β values for a series of compounds at very low concentrations in different solvents. First-order plots were obtained for all compounds. The reactions were followed by monitoring the change in the fluorescence intensity for all compounds. β values for these compounds are obtained by relating the relative values with an absolute value obtained previously for diphenylfuran. Absolute rate constants are then obtained by dividing these β values into the rate constant for the decay of singlet oxygen for each solvent. The data are recorded in Table V.

β values for 2-methyl-2-pentene, tetramethylethylene, and 2-methylfuran were carried out using the new method, outlined above. In the latter two cases methylene blue was used as the dye sensitizer and a filter fluorimeter with a Heathkit recorder was used to monitor the rate of disappearance of the diphenyliso-benzofuran in the quenching reactions.