Photooxidation of Isobenzofurans. A Dual Mechanism Process

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Abstract: The photooxidation of several substituted isobenzofurans has been studied. Kinetic behavior at low substrate concentrations shows that a second mechanism other than that involving singlet oxygen is operative, and the absence of azulene quenching demonstrates that the second mechanism involves direct addition of oxygen to excited singlet isobenzofuran. Rate constants for this singlet substrate–ground state oxygen reaction are in the range of 10^{10} M^{-1} sec^{-1} and the mechanism is calculated to contribute about 10% of the photooxidation at high isobenzofuran concentration, ranging upward to virtually 100% at lower substrate concentrations. The mechanism is suggested to be *via* charge-transfer rather than concerted addition and the possibility of such an oxidation mechanism is generalized to other aromatic systems.

A great deal of evidence has been amassed in the past few years to indicate that photoinduced addition of molecular oxygen to several types of substrates proceeds primarily if not exclusively *via* excited oxygen molecules in the ($^1\Delta_g$) electronic state.[2] In most such instances, the experimental observations are in accord with an energy-transfer mechanism involving substrate or sensitizer triplet states,[2,3a] but for molecules for which the intrinsic intersystem crossing quantum yield is near zero, it has been established that oxygen quenching of the excited singlet state of the substrate is the yield-limiting process.[3] This observation, though not inconsistent with the singlet oxygen mechanism, raises the possibility of alternative photooxidation mechanisms for highly fluorescent systems. Indeed, mesurements of competitive photooxidation of 1,3-diphenylisobenzofuran and tetramethylethylene led Wilson to suggest a second photooxidation mechanism, perhaps involving the substrate triplet state, for the isobenzofuran.[4]

We have recently undertaken to investigate in detail the primary photoprocesses for a series of substituted isobenzofurans and wish to report here experiments that demonstrate the presence of a second mechanism for isobenzofuran self-sensitized photoxidation in which electronically excited singlet state substrate molecules undergo direct reaction with ground state oxygen molecules. This second pathway also represents an alternative channel for oxygen-induced quenching of excited singlets besides that of induced intersystem crossing, namely, reactive quenching by oxygen.

Kinetic Analysis

The reactions which we consider for a substituted isobenzofuran (F) excited in the presence of oxygen are the following

$$\mathrm{F} + h\nu_e \longrightarrow {}^1\mathrm{F} \qquad (1)$$

$$^1\mathrm{F} \xrightarrow{k_f} \mathrm{F} + h\nu_f \qquad (2)$$

$$^1\mathrm{F} + \mathrm{O_2} \longrightarrow {}^3\mathrm{F} + \mathrm{O_2} \qquad (3)$$

$$^1\mathrm{F} + \mathrm{O_2} \xrightarrow{k_{\mathrm{sox}}} \mathrm{FO_2} \qquad (4)$$

$$^3\mathrm{F} + \mathrm{O_2} \longrightarrow \mathrm{F} + \mathrm{O_2}(^1\Delta_g) \qquad (5)$$

$$^3\mathrm{F} + \mathrm{O_2} \xrightarrow{k_{\mathrm{tox}}} \mathrm{FO_2} \qquad (6)$$

$$\mathrm{O_2}(^1\Delta_g) \longrightarrow \mathrm{O_2} \qquad (7)$$

$$\mathrm{O_2}(^1\Delta_g) + \mathrm{F} \xrightarrow{k_{\mathrm{oox}}} \mathrm{FO_2} \qquad (8)$$

This scheme allows for three possible mechanisms for photooxidation: *via* singlet substrate (k_{sox}), triplet substrate (k_{tox}), and singlet oxygen (k_{oox}). In other respects, it is substantially simpler than the full range of photoprocesses that could follow the initial excitation step, based on the following observations.

(i) As determined by our measurements (see below), the fluorescence quantum yields of isobenzofurans are sensibly unity in the absence of oxygen; hence, unimolecular internal conversion and intersystem crossing are negligible.

(ii) Previous work on a variety of systems indicates that oxygen quenching of singlets is primarily if not entirely an induced intersystem crossing not involving energy transfer to oxygen (process 3).[3a] In any event, should energy transfer be occurring, it would not alter the conclusions reached herein.

(iii) Oxygen quenching of triplets has been shown to proceed *via* energy transfer, and in solution the end result is oxygen molecules in the ($^1\Delta_g$) state.[2]

(iv) Bimolecular processes involving two F molecules (dimerization or excimer formation) are negligible at the concentrations used in this study ($<10^{-5}$ M substrate concentrations).

Following this scheme, one can write expressions for the yields of various species from their precursors: $\gamma_b{}^a$ = formation efficiency of species b from species a ($\Delta = \mathrm{O_2}(^1\Delta_g)$; $1 = {}^1\mathrm{F}$; $3 = {}^3\mathrm{F}$).

$$\gamma_{\mathrm{FO_2}}{}^1 = k_{\mathrm{sox}}[\mathrm{O_2}]\{k_f + (k_{\mathrm{sox}} + k_3)[\mathrm{O_2}]\}^{-1} \qquad (9)$$

$$\gamma_3{}^1 = k_3[\mathrm{O_2}]\{k_f + (k_3 + k_{\mathrm{sox}}[\mathrm{O_2}]\}^{-1} \qquad (10)$$

$$\gamma_{\mathrm{FO_2}}{}^3 = k_{\mathrm{tox}}(k_{\mathrm{tox}} + k_5)^{-1} \qquad (11)$$

$$\gamma_\Delta{}^3 = k_5(k_{\mathrm{tox}} + k_5)^{-1} \qquad (12)$$

$$\gamma_{\mathrm{FO_2}}{}^\Delta = k_{\mathrm{oox}}[\mathrm{F}](k_7 + k_{\mathrm{oox}}[\mathrm{F}])^{-1} \qquad (13)$$

The quantum yield for photooxidation will then depend on the yields of these various species.

$$\phi_{\mathrm{FO_2}} = \gamma_{\mathrm{FO_2}}{}^1 + \gamma_3{}^1\gamma_{\mathrm{FO_2}}{}^3 + \gamma_3{}^1\gamma_\Delta{}^3\gamma_{\mathrm{FO_2}}{}^\Delta \qquad (14)$$

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[1] This work constituted a portion of the M.S. degree requirements of Mr. T. Akashah.

[2] For a comprehensive review, see D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).

[3] B. Stevens and B. E. Algar, *Ann. N. Y. Acad. Sci.*, **171**, 50 (1970); B. E. Algar and B. Stevens, *J. Phys. Chem.*, **74**, 3029 (1970), and references cited therein; (b) R. Livingston and V. S. Rao, *ibid.*, **63** 794 (1959).

[4] T. Wilson, *J. Amer. Chem. Soc.*, **88**, 2898 (1966).

For air-saturated solutions, all of these yields are independent of substrate concentration except for $\phi_{FO_2}{}^{\Delta}$, which will decrease with decreasing substrate concentration due to the unimolecular decay of oxygen back to the ground state (k_7). At sufficiently low concentrations, the third term in eq 14 may become negligible compared with the other two, rendering ϕ_{FO_2} concentration independent. In that case, the rate of disappearance of substrate will depend only on the number of photons absorbed per second, or, in terms of solution transmittance T and rate of photon incidence I_0

$$-\mathrm{d}[F]/\mathrm{d}t = \phi_{FO_2}(1 - T)I_0 \qquad (15)$$

If transmittance is replaced by absorbance and series expansion performed

$$-\mathrm{d}[F]/\mathrm{d}t = (1 - e^{-2.3A})I_0\,\phi_{FO_2} = (1 - 1 + 2.3A\ \ldots)I_0\phi_{FO_2} \qquad (16)$$

From this expression, assuming constant photon flux and solution absorbance that is low enough to justify truncating the series, the photooxidation process should follow first-order kinetics.

$$-\mathrm{d}[F]/\mathrm{d}t = 2.3\epsilon b[F]\phi_{FO_2}I_0 \qquad (17)$$

The change of concentration of F with time can be followed easily by monitoring the fluorescence intensity of the sample, which is readily observed even at concentrations as low as 10^{-8} M. A knowledge of the initial absorbance of the solution and actinometric determination of photon flux then permits ϕ_{FO_2} to be determined from first-order plots.

Under conditions where first-order kinetics obtain, the quantum yield so determined may be due entirely to excited singlets (k_{sox}), due entirely to excited triplets (k_{tox}), or due to a combination of the two. The contribution of k_{tox} can be assessed by determining ϕ_{FO_2} in the presence of a known triplet state quencher such as azulene.[3a] In the presence of such a quencher, $\phi_{FO_2}{}^3$ becomes quencher concentration dependent.

$$\gamma_{FO_2}{}^3 = k_{tox}[O_2]\{(k_{tox} + k_5)[O_2] + k_q[A]\}^{-1} \qquad (18)$$

The extent of diminution of ϕ_{FO_2} by added azulene thus gives the relative importances of k_{sox} and k_{tox}.

Photosensitized oxidation of substrate utilizing a photosensitizer whose singlet state is not quenched by oxygen follows a substantially simpler kinetic scheme due to the absence of excited singlet and triplet states of the substrate.

$$S + h\nu_e \longrightarrow {}^1S \qquad (19)$$

$${}^1S \longrightarrow S \qquad (20)$$

$${}^1S \longrightarrow {}^3S \qquad (21)$$

$${}^3S + O_2 \longrightarrow S + O_2({}^1\Delta_g) \qquad (22)$$

$$F + O_2({}^1\Delta_g) \xrightarrow{k_{oox}} FO_2 \qquad (8)$$

$$O_2({}^1\Delta_g) \longrightarrow O_2 \qquad (7)$$

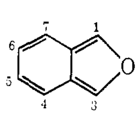
For this scheme, the quantum yield of peroxide is

$$\phi_{FO_2} = \frac{k_{21}}{(k_{20} + k_{21})}\frac{k_{oox}[F]}{k_7 + k_{oox}[F]} = \gamma_{IS}\frac{k_{oox}[F]}{k_7} \qquad (23)$$

where γ_{IS} is the triplet yield of sensitizer and $k_{oox}[F]$ is assumed to be small relative to k_7.

Experimental Section

The following substituted isobenzofurans were prepared according to known synthetic procedures: 1,3-diphenyl-5,6-dimethylisobenzofuran (DPDMI),[5] 1,3,4,7-tetraphenylisobenzofuran (TPI),[6] and hexaphenylisobenzofuran (HPI).[7] In addition, 2,5-diphenylfuran (DPF) was prepared,[8] and all of these compounds as well as commercially obtained 1,3-diphenylisobenzofuran (DPI) (Aldrich) were purified by chromatography on alumina or fluorisil, using benzene solvent under dim light conditions. Analytical or spectrograde benzene, methanol, and ethanol were each purified by fractional distillation, after which they showed no measurable fluorescent impurities.



isobenzofuran

Fluorescence quantum yields were determined on a Baird-Atomic Model SF-1 Fluorispec fluorescence spectrophotometer whose cell compartment was modified to include a rhodamine B quantum counter solution viewed by an IP-28 photomultiplier tube. Quantum yields were determined relative to zone-refined anthracene and chromatographed 9,10-diphenylanthracene following quantum counter procedures described by Parker[9] and general precautions recommended by Demas and Crosby.[10] Absorption spectra of these solutions were obtained with a Perkin-Elmer 202 uv-vis spectrophotometer.

Self-sensitized photooxidation kinetics runs were carried out using the 404-nm output of a 100-W short arc mercury lamp filtered by Corning filters CS 7-51 and 3-75. Fluorescence from these solutions was monitored at 450 nm by a $^1/_4$ meter Jarrell-Ash monochromator equipped with photomultiplier tube, picoammeter, and strip-chart recorder.

Dye-sensitized photooxidations were carried out using the 546-nm output of the 100-W mercury lamp filtered by Corning CS 3-69 and 4-96 filters and were done in the sample compartment of the fluorispec with continuous monitoring of solution fluorescence at excitation and fluorescence wavelengths selected to minimize inner filter effects.

Actinometry at 404 nm was by means of the ferrioxalate chemical actinometer,[11] while at 546 nm the Reinecke's salt chemical actinometer was used.[12] Corrections were made for the small fraction of 585-nm light transmitted by the filters in photosensitization runs. Optical densities of stock solutions of substrate and of actinometric solutions were determined using a Beckman Model B spectrophotometer.

Results and Discussion

The results of our several experiments on substituted isobenzofurans are collected together in Table I, which includes both yield values and values for various rate constants derived therefrom. In the main, the values reported have been determined in benzene solution, with the exception of the singlet oxygen oxidation rate constants (k_{oox}). The latter are derived from sensitized oxidation experiments in which methanol solvent was used in order to have a reliable value of the sensitizer triplet yield. The determinations of ϕ_{FO_2}, from which k_{sox} is derived, were made both in benzene and in methanol with results which were nearly identical except in the case of DPDMI (see

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Table I. Yield and Rate Parameters for Photooxidation of Substituted Isobenzofurans[a]

Parameter	DPI[b]	DPDMI[c]	TPI[d]	HPI[e]
ϕ_f[f]	0.96	0.94	0.96	0.95
ϕ_q[g]	0.12_3	0.12_0	0.13_1	0.12_3
$\phi_{FO_2}{}^F$[h]	0.0075 0.0089 (M)	0.027 0.018 (M)	0.030 0.032 (M)	0.023 0.027 (M)
$\phi_{FO_2}{}^3$[i]	<0.0001			
k_f, $sec^{-1} \times 10^{-8}$[j]	3.1	3.6	2.9	3.1
k_{sox}, $M^{-1} sec^{-1} \times 10^{-8}$[k]	18	75	69	56
k_{oox}, $M^{-1} sec^{-1} \times 10^{-8}$[l]	6.13 (M)	5.24 (M)	6.62 (M)	6.88 (M)

[a] In benzene solution, except values marked (M) which are in methanol. [b] 1,3-Diphenylisobenzofuran. [c] 1,3-Diphenyl-5,6-dimethylisobenzofuran. [d] 1,3,4,7-Tetraphenylisobenzofuran. [e] 1,3,-4,5,6,7-Hexaphenylisobenzofuran. [f] Fluorescence quantum yield, in deaerated solution, 355–405 nm, relative to $\phi_f = 1.00$ for 9,10-diphenylanthracene in benzene. [g] Yield of oxygen quenching of fluorescence in air-saturated solution. [h] Concentration-independent photooxidation product yield. [i] Concentration independent photooxidation product yield attributable to triplet substrate. [j] Fluorescence rate constant derived from ϕ_q. [k] Rate constant for $^1F + O_2(^3\Sigma_g^-) \rightarrow FO_2$ reaction derived from $\phi_{FO_2}{}^F$. [l] Rate constant for $F + O_2(^1\Delta_g) \rightarrow FO_2$ reaction, from sensitized results.

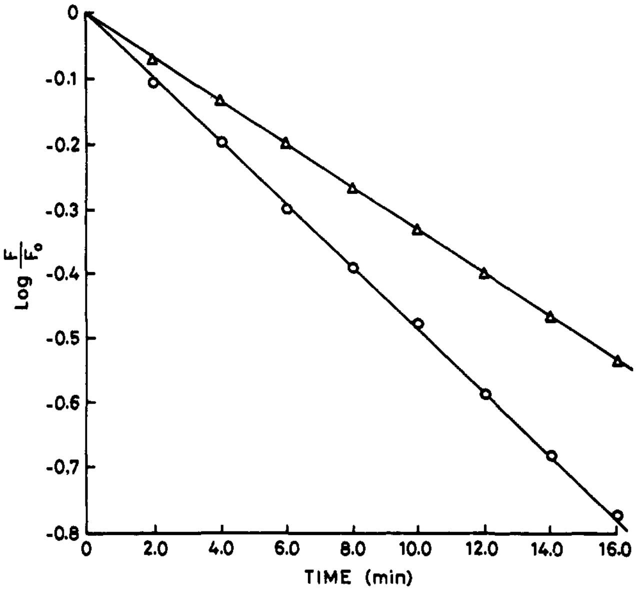

Figure 1. Self-sensitized photooxidation of DPDMI in the low concentration region ($[DPDMI]_0 = 9.7 \times 10^{-7}$ M): (○) benzene solution, (△) methanol solution.

Figure 1), where the yield in benzene was 50% higher than that in methanol. Extinction coefficient and absorption spectrum measurements for the isobenzofurans yielded virtually identical results for the two solvents also, from which we conclude that k_f and k_{sox} (except for DPMDI) are comparable in these solvents. Comparability of the second-order rate constants is to be expected in view of the very similar viscosities of methanol and benzene while the insensitivity of k_f to solvent polarity is in agreement with earlier spectral measurements in benzene and dimethylformamide.[5,13]

Fluorescence quantum yields reported here are relative to $\phi_f = 1.0$ for 9,10-diphenylanthracene in benzene and are constant between 350 and 400 nm. Berlman has, somewhat arbitrarily, adopted the value 1.0 for 9,10-DPA in cyclohexane;[14] Birks and Dyson, as a result of a set of relative determinations, assigned a quantum yield of 0.85 in benzene.[15] We have measured the quantum yields of anthracene in benzene and quinine bisulfate in 0.1 N H_2SO_4 relative to a yield of 1 for 9,10-DPA in benzene over the 350–375 nm range and find $\phi_{AN} = 0.23$ (lit. 0.27) and $\phi_{QB} = 0.58$ (lit. 0.546). Our measurements therefore favor the value of unity.

These quantum yields are those of isobenzofurans when second-order quenching processes are absent, *i.e.*, for oxygen-free solutions. In air-saturated solutions, fluorescence quenching is observed with yields as indicated in Table I (ϕ_q). It has been established that oxygen quenching proceeds with a diffusion-controlled rate constant for a large variety of compounds, as a result of which reliable estimates of k_f can be made from oxygen-quenching data.[2,14,16] Fluorescence rate constants derived from the oxygen quenching yields are also collected in Table I. The values are typical of strongly allowed (π,π^*) type excitations. This fact, the insensitivity of excited state parameters to solvent polarity, and the absence of significant intersystem crossing indicate the (π,π^*) nature of the excited singlet state, insignificantly perturbed by any nearby (n,π^*) state, and strongly imply that the lowest triplet state of the isobenzofurans is also (π,π^*) in nature with the $^3(n,\pi^*)$ state higher in energy than the $^1(\pi,\pi^*)$ excited state.[17]

A typical first-order plot for the low concentration self-sensitized photooxidation process is shown in Figure 1 for DPDMI. That the reaction observed under these conditions is oxidation was verified by irradiating a solution of DPI under similar conditions but with oxygen removed by evacuation and freeze–thaw techniques. A small residual reaction was observed, most likely due to incomplete removal of oxygen, but virtually all of the photoreactivity of the air-saturated solution was absent. Dark autooxidation at these low concentrations was shown to be negligible by constancy of the fluorescence intensity after storage of 10^{-5} M solutions in the dark for 48 hr.

As described above, yield values from slopes of these plots may be a composite of singlet substrate and triplet substrate contributions. The degree of triplet substrate participation was assessed by measuring photooxidation yields for DPI in the presence of azulene, which is known to quench triplet states with a diffusion-controlled rate.[18]

Wilson[4] has suggested that a cage effect, in which reactions 3, 5, and 8 all proceed within the solvent cage thereby precluding quenching of the DPI triplet state, might also be responsible for her observations. In that event, azulene would be unable to quench the singlet-oxygen-induced photooxidation process. To check this possibility, the photooxidation of 10^{-3}

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(13) A. Zweig, G. Metzler, A. Maurer, and B. G. Roberts, *J. Amer. Chem. Soc.*, **89**, 4091 (1967).

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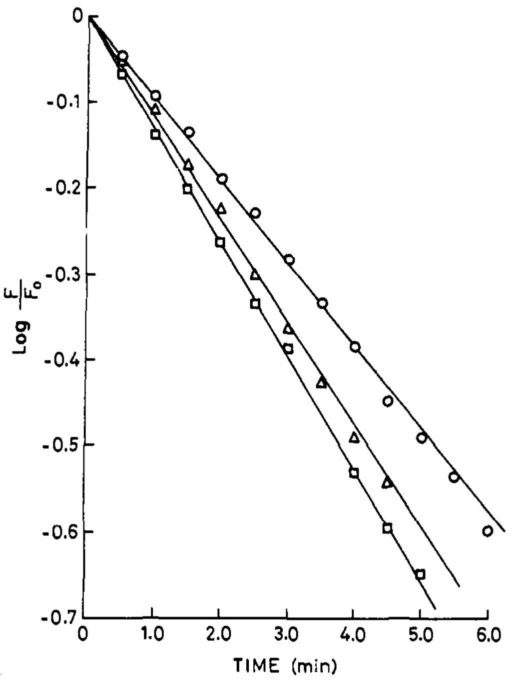

Figure 2. Rose Bengal sensitized photooxidation of isobenzofurans in methanol solution at low concentrations: (○) DPDMI, $C_0 = 3.0 \times 10^{-6}$ M; (△) TPI, $C_0 = 5.3 \times 10^{-6}$ M; (□) HPI, $C_0 = 9.2 \times 10^{-6}$ M. Sensitizer concentration was 7.0×10^{-7} M in all cases.

M DPI solutions was compared with that of 10^{-3} M DPI-10^{-3} M azulene solutions, under conditions where only DPI absorbs (404-nm Hg line). It was found that azulene does indeed quench the photoreaction, indicating that triplet DPI does diffuse out of the solvent cage in which it is first formed.

Results of azulene quenching at low substrate concentration, collected in Table II, indicate that the quantum yield of photooxidation products from triplet substrate is less than 10^{-4}. Using the literature values for oxygen quenching of triplet states[2] ($k_5 = 2.0 \times 10^9$ M^{-1} sec^{-1}), for azulene quenching of triplets[3a] ($k_q = 1.0 \times 10^{10}$ M^{-1} sec^{-1}), and for solubility of oxygen in benzene[19] ($[O_2] = 1.43 \times 10^{-3}$ M), this observation yields an upper limit for the triplet reaction rate constant, $k_{tox} \leqq 7 \times 10^6$ M^{-1} sec^{-1}.

Table II. Effect of Azulene on Photooxidation Yields[a]

[A], $M \times 10^3$	$\phi_{FO_2}{}^F$
0.00	0.0075
0.10	0.0074
0.50	0.0072
1.00	0.0074

[a] First-order region: [DPI] = 6.1×10^{-7} M.

As a result of these measurements, it can be concluded that the concentration-independent quantum yields observed for isobenzofurans at low substrate concentrations are due entirely to the singlet substrate reaction path: $\phi_{FO_2} = \gamma_{FO_2}{}^1$. From these values, values of k_f given in Table I, and the oxygen concentration value, values of k_{sox} can thus be obtained; these are also indicated in the table. From oxygen solubility data for methanol,[19] k_{sox} values for that solvent are obtained which are the same within experimental error as those in benzene, save for DPDMI, for which there appears to be a real and unexplained solvent effect.

To determine the yield of photoproducts arising from the singlet oxygen reaction, two possible methods were considered: measurements in the high concentration limit where $\gamma_{FO_2}{}^\Delta$ would be dominant, or photooxidation by means of a sensitizer to eliminate excited substrate molecules. Both present difficulties, but the sensitization technique was chosen here to avoid the necessity of very high photon fluxes and serious inner filter and inhomogenity effect corrections that would have been required for high concentration self-sensitized photooxidation experiments.

We have chosen to use Rose Bengal in methanol as sensitizer for these experiments, inasmuch as it is a thoroughly studied system with high triplet yield ($\gamma_{IS} = 0.76$) and negligible oxygen quenching of the singlet[20] and has an absorption maximum which coincides with the mercury emission line at 546 nm. Substrate concentrations were kept below 10^{-6} M and first-order kinetic behavior as predicted by eq 23 was observed (Figure 2). From the slopes of these curves, actinometric measurements, and values of k_7 ($^1\Delta_g$ decay rate) determined by Merkel and Kearns,[21] values of k_{oox} were obtained as reported in Table I. The value of k_{oox}/k_7 obtained for DPI in these experiments (4.41×10^3 M^{-1}) is in good agreement with the value of Merkel and Kearns (5×10^3), obtained by an entirely different technique.

From the results of this study, we find that the general quantum yield expression given above (eq 14) can be simplified to give

$$\phi_{FO_2} = \gamma_{FO_2}{}^1 + \gamma_3{}^1\gamma_{FO_2}{}^\Delta \quad (24)$$

or, assuming that quenching of singlet substrate by oxygen yields either peroxide product or triplet substrate

$$\phi_{FO_2} = \phi_{FO_2}{}^F + (\phi_q - \phi_{FO_2}{}^F)k_{oox}[F] \times (k_7 + k_{oox}[F])^{-1} \quad (25)$$

This expression can be used to assess the importance of the two photooxidation mechanisms. At concentrations of 10^{-3} M and above, where $k_{oox}[F] \gg k_7$, the relative contributions are given simply by the fractions of singlet substrate quenched by oxygen to peroxide and to triplet state, respectively, or about 7 and 93% for DPI. As the substrate concentration falls, the singlet oxygen mechanism becomes progressively less important, falling to 80% at 10^{-4} M and 35% at 10^{-6} M (these values will, however, be strongly solvent dependent owing to the solvent dependence of k_7[22]), until at concentrations of 10^{-6} M or lower essentially all of the reaction proceeds *via* excited substrate oxidation. The above assessment is in qualitative agreement with Wilson's estimate[4] that for 10^{-3} M DPI in pyridine at least 75% of the reaction is due to singlet oxygen.

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[22] P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 1029 (1972).

The existence of two pathways for photooxidation raises the possibility of different intermediates and different final products of the overall processes. Although it is difficult to envisage products other than the endoperoxide from either pathway, we have searched spectroscopically for evidence of different products by completely photooxidizing solutions differing 100-fold in initial substrate concentration and then comparing product uv absorption spectra. At high initial concentration, the singlet oxygen pathway is responsible for more than 80% of the product, whereas at low concentration over 80% derives from the singlet substrate path. In spite of this, the uv absorption spectrum of the product, both in cyclohexane and in methanol solvents, was exactly the same from high initial substrate concentration (suitably diluted after irradiation) as from low. Spectroscopic evidence thus indicates that the photoproduct is the same from the two pathways.

For the singlet oxygen reaction with dienes, in which class the isobenzofurans fall, orbital and state correlation diagrams predict that the concerted reaction is allowed.[2] The correlation for the excited substrate plus triplet oxygen reaction is substantially more complex to interpret, since each reactant possesses a pair of singly occupied molecular orbitals. However, since the ground state molecules correlate with the first triplet state of the product, the excited substrate plus triplet oxygen must correlate with some higher triplet state, and it would appear necessary for this triplet to involve excitation of two electrons. We believe that this is likely to be energetically disfavored; in addition, the very high rate constants observed for the reaction imply minimal orientation requirements in the reaction complex and a concerted addition reaction is thus unlikely. An attractive possibility is a charge-transfer complex, such as has been proposed for oxygen quenching of fluorescence.[23,24] The oxygen-quenching reaction for excited singlet isobenzofurans is then

$$\begin{array}{l} \mathrm{F} + \mathrm{O_2} \longrightarrow (\mathrm{F^+} \cdots \mathrm{O_2^-}) \longrightarrow {}^3\mathrm{F} + \mathrm{O_2} \\ \qquad\qquad\qquad\qquad\qquad\;\; \longrightarrow \mathrm{FO_2} \end{array}$$

This scheme could equally well apply to other oxidizable substrate molecules which can undergo charge-transfer quenching. We have examined the highly fluorescent compound 2,5-diphenylfuran ($\phi \geqq 0.90$) for which we found some evidence for the reaction but with a much smaller rate constant ($k_{\mathrm{sox}} \sim 10^7$ M^{-1} sec^{-1}). However, 2,5-diphenylfuran rather surprisingly turns out to be quite resistant to oxidation by either mechanism ($k_{\mathrm{oox}} \sim 5 \times 10^5$ M^{-1} sec^{-1}); its low k_{sox} value may be due entirely to this stability. The 9,10-substituted anthracenes are compounds for which there is a certain amount of disagreement in the literature concerning reactivity toward singlet oxygen[3a,25] as well as a report of singlet substrate participation (interpreted as quenching to give singlet oxygen).[3b] Reexamination of the photooxidation of these compounds including possible participation of singlet substrate appears to be desirable.

Further evidence concerning the generality of the k_{sox} reaction is provided by quenching studies on aromatics carried out by Potashnik, Goldschmidt, and Ottolenghi,[26] in which it was ascertained that the triplet substrate yield from oxygen fluorescence quenching was close to unity for several catacondensed aromatic hydrocarbons. On the other hand, for pyrene and phenanthrene in acetonitrile, triplet yields closer to 0.5 were obtained, indicating a competing quenching path that could possibly be reactive quenching. Since the limits of error reported were ±0.11, a 10% reactive quenching contribution (the same order of magnitude observed by us for DPI) cannot be ruled out for any of these compounds.

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