Factors Governing the Efficiency of Singlet Oxygen Production during Oxygen Quenching of Singlet and Triplet States of Anthracene Derivatives in Cyclohexane Solution

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Abstract: The efficiencies of singlet oxygen production from the first excited singlet and triplet states of a range of substituted anthracenes in cyclohexane are reported. For all of the anthracene derivatives in this solvent, the efficiency of singlet oxygen production from the triplet state, f_Δ^T, is found to be unity. In contrast, however, the efficiency of singlet oxygen production from the first excited singlet state, f_Δ^S, varies from zero for anthracene to unity for 9,10-dicyanoanthracene. It is established that the magnitude of f_Δ^S is determined by the same factors which govern intersystem crossing yields for anthracene derivatives, i.e., the activation energy for intersystem crossing to higher triplet states. In addition it is confirmed that oxygen quenching of the excited singlet states of four anthracene derivatives in cyclohexane proceeds exclusively via enhanced intersystem crossing yielding triplet states. Some previously unavailable photophysical data are also reported for these substituted anthracenes, i.e., triplet energies, triplet yields, and rate constants for oxygen quenching of triplet states.

Introduction

There has been considerable recent interest in factors which determine oxygen quenching of excited states and the efficiency of formation thereby of singlet oxygen.[1–13] However, despite intense research over the last 30 years, the mechanism by which oxygen quenches the excited states of organic molecules remains poorly understood.[1–16] It is well-known that singlet oxygen $O_2{}^*({}^1\Delta_g)$ is frequently produced as a consequence of these quenching interactions. However, it is abundantly clear that the yield of singlet oxygen and the quenching rate constants vary considerably depending on the nature of the excited state being quenched and on the solvent or microenvironment.[1–16]

The quantum yield of sensitized production of singlet oxygen, ϕ_Δ, is given by the sum of the contributions arising from oxygen quenching of the lowest excited singlet state (S_1) and the lowest excited triplet state (T_1) of the sensitizer, i.e.

$$\phi_\Delta = \phi_\Delta(S_1) + \phi_\Delta(T_1) \tag{1}$$

The various competing reactions can be understood by considering Scheme I (shown below) for a hydrocarbon ^1M excited to singlet and triplet states, $^1M^*$ and $^3M^*$, respectively.

Scheme I

$$^1M + h\nu \rightarrow {}^1M^*$$

1. $$^1M^* \xrightarrow{k_F} {}^1M + h\nu_F$$

2. $$^1M^* \xrightarrow{k_{ic}} {}^1M$$

3. $$^1M^* \xrightarrow{k_{isc}} {}^3M^*$$

4. $$^1M^* + {}^3O_2 \xrightarrow{k_{S\Delta}} {}^3M^* + {}^1O_2{}^*$$

5. $$^1M^* + {}^3O_2 \xrightarrow{k_{ST}} {}^3M^* + {}^3O_2$$

6. $$^1M^* + {}^3O_2 \xrightarrow{k_{SO}} \text{quenching}$$

7. $$^3M^* \xrightarrow{k_D^T} {}^1M$$

8. $$^3M^* + {}^3O_2 \xrightarrow{k_{T\Delta}} {}^1M + {}^1O_2{}^*$$

9. $$^3M^* + {}^3O_2 \xrightarrow{k_{TO}} \text{quenching}$$

from which it follows that

$$\phi_F^O = \frac{k_F}{k_F + k_{ic} + k_{isc}} \quad \text{and} \quad \phi_T^O = \frac{k_{isc}}{k_F + k_{ic} + k_{isc}} \tag{2}$$

where ϕ_F^O and ϕ_T^O are the quantum yields of fluorescence and of triplet state production in the absence of oxygen, respectively. Quencing of the excited singlet state by oxygen leads to a Stern–Volmer relationship between the fluorescence quantum yields in the absence and presence of oxygen as given by eq 3 where F^O and F represent the fluorescence intensities of the sensitizer in the absence and presence of oxygen, i.e.

$$\frac{\phi_F^O}{\phi_F} = \frac{F^O}{F} = 1 + k_S^{O_2}[O_2]/k_D^S \tag{3}$$

where $k_S^{O_2} = k_{S\Delta} + k_{ST} + k_{SO}$, $k_D^S = k_F + k_{ic} + k_{isc}$, and we can

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define the fraction of singlet states quenched by oxygen as

$$P_S^{O_2} = k_S^{O_2}[O_2]/(k_D^S + k_S^{O_2}[O_2]) = (F^O - F)/F^O \qquad (4)$$

The quantum yield of triplet state production in the presence of oxygen ($\phi_T^{O_2}$) is given by eq 5

$$\phi_T^{O_2} = \phi_T^O(1 - P_S^{O_2}) + f_T^{O_2}P_S^{O_2} \qquad (5)$$

where $f_T^{O_2}$ is the fraction of singlet states quenched by O_2 which yield triplet states. Note that step 6 in the mechanism represents quenching of the singlet state by oxygen by any route which does not produce either singlet oxygen or triplet state, i.e., other than those shown in steps 4 and 5. Substitution of eqs 4 and 5 into eq 1 gives

$$\phi_\Delta = f_\Delta^{\mathcal{S}}P_S^{O_2} + \phi_T^{O_2}f_\Delta^{\mathcal{T}}P_T^{O_2} \qquad (6)$$

where $f_\Delta^{\mathcal{S}}$ and $f_\Delta^{\mathcal{T}}$ are defined as the fraction of S_1 states and the fraction of T_1 states, respectively, quenched by oxygen which give $O_2^*(^1\Delta_g)$. $P_T^{O_2}$ equals that fraction of the triplet states which are quenched by oxygen thus

$$P_T^{O_2} = \frac{k_T^{O_2}[O_2]}{k_D^T + k_T^{O_2}[O_2]} \qquad (7)$$

where $k_T^{O_2} = k_{T\Delta} + k_{TO}$.

Since triplet states are usually quite long lived and oxygen quenching is usually very efficient, $P_T^{O_2}$ in the presence of air is often close to unity. When $P_T^{O_2} = 1$ combining eqs 3–6 gives

$$\phi_\Delta\frac{F^O}{F} = (f_\Delta^{\mathcal{S}} + f_T^{O_2}f_\Delta^{\mathcal{T}})\left[\frac{F^O}{F} - 1\right] + \phi_T^O f_\Delta^{\mathcal{T}} \qquad (8)$$

which can be used to obtain information concerning the determining factors $f_\Delta^{\mathcal{S}}$, $f_\Delta^{\mathcal{T}}$, and $f_T^{O_2}$. However, independent measurements of ϕ_T^O and $f_T^{O_2}$ are required to separately determine $f_\Delta^{\mathcal{S}}$ and $f_\Delta^{\mathcal{T}}$.

In a recent compilation we listed over 1400 values of ϕ_Δ in fluid solution together with 357 values for $f_\Delta^{\mathcal{T}}$, but only 28 values for $f_\Delta^{\mathcal{S}}$.[10] We have recently shown that for a series of substituted naphthalenes in benzene the efficiency of singlet oxygen production from triplet states, $f_\Delta^{\mathcal{T}}$, increases with the oxidation potential of the naphthalene derivative.[11] In addition we demonstrated that $k_T^{O_2}$ shows an inverse correlation with the oxidation potential of the naphthalene derivative being quenched which is evidence for the participation of charge transfer interactions within excited state/oxygen complexes formed during the quenching process. In the present study we report the efficiencies of singlet oxygen generation $f_\Delta^{\mathcal{S}}$ and $f_\Delta^{\mathcal{T}}$ for a series of anthracene derivatives in cyclohexane.

Experimental Section

Materials. Anthracene, 9,10-dimethylanthracene, and 9,10-diphenylanthracene (Aldrich) and cyclohexane (Aldrich spectrophotometric grade) were used as received; phenazine, 9-chloroanthracene, and 9-phenylanthracene (Aldrich) and 9,10-dichloroanthracene, 9-methylanthracene, and 9-bromoanthracene (Eastman Kodak) were recrystallized from ethanol; 9,10-dibromoanthracene and 9-cyanoanthracene (Aldrich) and 9,10-dicyanoanthracene (Kodak) were recrystallized from benzene; 9-methoxyanthracene was a gift from the late E. J. Bowen which was recrystallized from ethanol.

Apparatus. Absorption spectra were recorded with a Phillips PU8800 spectrophotometer and singlet excited state energies were determined from the position of the 0,0 absorption bands (see Figure 1). Triplet energies were measured using the method developed by Evans[17] in which use is made of the enhancement of singlet–triplet absorption by a high pressure of oxygen, typically 80 atm. Since there is little or no overlap of charge transfer absorption with the enhanced singlet–triplet absorption in the case of anthracene derivatives in the presence of high pressures of oxygen, triplet energies could simply be determined from the position of the 0,0 bands. Representative spectra are shown in Figure 2. Fluorescence measurements were carried out using a Perkin Elmer LS4 spectrophotofluorimeter.

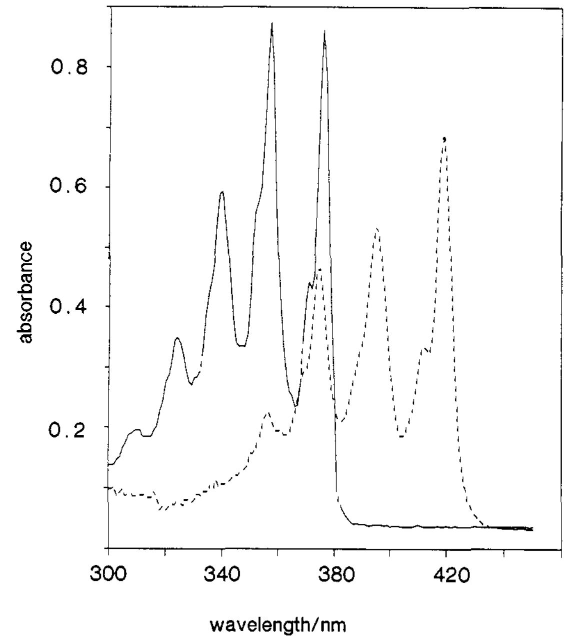

Figure 1. Absorption spectra of anthracene (—) and 9,10-dicyanoanthracene (- - -) in cyclohexane.

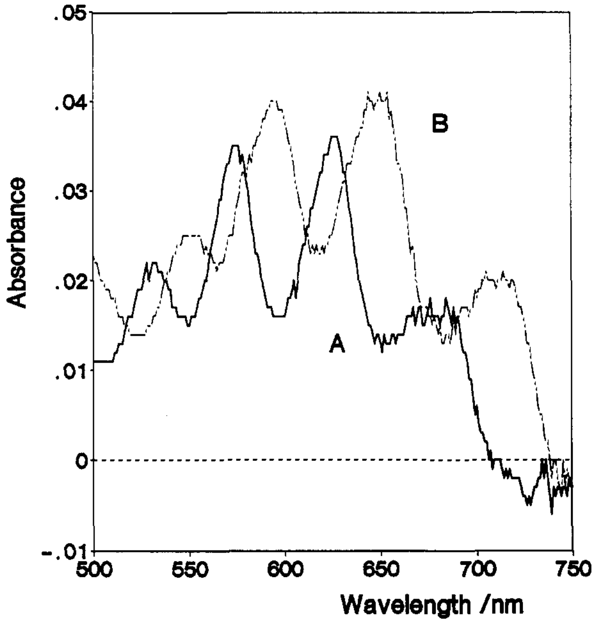

Figure 2. Oxygen-enhanced $S_0 \rightarrow T_1$ absorption spectra in carbon tetrachloride: (A) 9,10-dimethylanthracene and (B) 9-phenylanthracene.

Transient absorption measurements were obtained using a nanosecond laser flash photolysis system with right angle geometry as described elsewhere.[18] Excitation was with 8-ns 355-nm pulses from a Lumonics HY200 Q-switched neodymium-YAG laser. Emission from singlet oxygen following laser excitation was detected by time resolved spectroscopy as described previously.[11] For $f_\Delta^{\mathcal{S}}$ and $f_\Delta^{\mathcal{T}}$ measurements, air was removed from the solutions by 3 freeze–pump–thaw cycles followed by equilibration with pure oxygen at pressures up to 3 atm. For each determination six different concentrations of oxygen were used and for each of these solutions the steady state fluorescence intensity was measured. The intensity of singlet oxygen phosphorescence (P_0) at time $t = 0$ was obtained by fitting the decay curve to a single exponential function. A set of P_0 values were obtained for different laser intensities and plots of P_0 vs relative laser

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intensity were linear for pulse energies of up to 0.5 mJ per pulse. The ϕ_Δ values were determined relative to the slope obtained for the plot of P_0 vs relative laser intensity for *p*-methoxyacetophenone/naphthalene in air saturated cyclohexane for which a value of 0.92 has been measured.[19]

Triplet quantum yields of anthracene and 9-methylanthracene were determined using the method of Wilkinson et al.[20] in which the fluorescence quenching and the enhanced triplet–triplet absorption of these hydrocarbons caused by the addition of various amounts of xenon were monitored. Thus solutions degassed by the freeze–pump–thaw method were equilibrated with different amounts of xenon added by freezing from the vacuum line. Triplet–triplet absorption was measured at 430 nm and initial triplet–triplet absorbances were obtained by fitting the decay curve to a monoexponential function. These initial absorbance values were plotted against laser intensity which was varied and linear plots were observed. In the presence of xenon as a heavy atom quencher the following process occurs.

$$10. \qquad {}^1M^* + Xe \xrightarrow{k_S^{Xe}} {}^3M^* + Xe$$

If we consider steps 1–3 in Scheme I together with step 10, it follows that the quantum yield of triplet state production in the presence of xenon, ϕ_T^{Xe}, is given by

$$\phi_T^{Xe} = \phi_T^O(1 - P_S^{Xe}) + P_S^{Xe} \tag{9}$$

where P_S^{Xe} is the fraction of singlet states quenched by xenon. The ratio of the triplet yield in the absence and presence of xenon is equal to the ratio of the initial triplet absorbances measured in the absence and presence of xenon, i.e.

$$\frac{\phi_T^O}{\phi_T^{Xe}} = \frac{A_T^O}{A_T^{Xe}} \tag{10}$$

and since P_S^{Xe} can be calculated from the fluorescence intensity ratio for quenching by xenon, i.e.

$$P_S^{Xe} = \frac{F^O - F}{F^O} \tag{11}$$

rearrangement gives eq 12 (see ref 20).

$$\frac{F^O}{F} - 1 = \phi_T^O\left[\frac{A_T^{Xe}F^O}{A_T^O F} - 1\right] \tag{12}$$

Values of ϕ_T^O were determined from the slopes of plots of $(F^O/F) - 1$ against $((F^O/F)(A_T^{Xe}/A_T^O) - 1)$ (see Figure 3).

The rate constants for oxygen quenching of triplet states were determined by fitting the decay curves of triplet–triplet absorption to single exponential functions and using eq 13

$$k_T^{O_2} = (k_a - k_D^T)/[O_2] \tag{13}$$

where k_a and k_D^T are the first-order decay constant under air and under vacuum, respectively, and $[O_2]$ is the oxygen concentration in cyclohexane taken as 2.1×10^{-3} mol dm^{-3} (see ref 21). From the ratio of the triplet absorbances at time $t = 0$, values of $f_T^{O_2}$ were measured using the following equation which is obtained by reorganizing eqs 3–5

$$f_T^{O_2} = \phi_T^O\left(\frac{A_T^{O_2}}{A_T^O} - \frac{F}{F^O}\right)\Big/\left(1 - \frac{F}{F^O}\right) \tag{14}$$

where $A_T^{O_2}$ and A_T^O are the triplet absorbances in the presence and absence of oxygen, which are directly proportional to $\phi_T^{O_2}$ and ϕ_T^O, respectively.

Results and Discussion

The photophysical properties of anthracene and its derivatives are collected in Table I. These demonstrate that the energy difference between the lowest singlet and lowest triplet states is in all cases greater than 94 kJ mol^{-1} and that therefore it is energetically possible to produce $O_2^*(^1\Delta_g)$ by oxygen quenching of both singlet and triplet states in the case of these anthracene derivatives. Although substituent effects on the singlet state energies of anthracene derivatives are well documented,[26,27] there have been few systematic measurements for triplet states. However, it is apparent (Table I) that the substituent shifts on T_1 are about one-half as large as those for S_1. It is also apparent

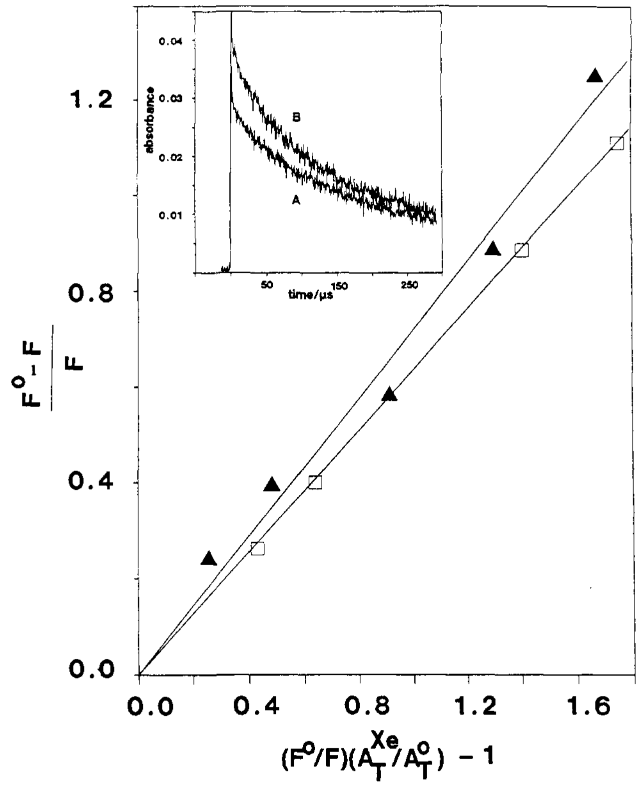

Figure 3. Plots for determination of triplet quantum yields using xenon as a heavy atom quencher of fluorescence. The insert shows T–T absorption of anthracene in cyclohexane at 430 nm in the absence (A) and presence (B) of xenon: (▲) anthracene and (□) 9-methylanthracene.

Table I. Energies of Singlet (E_S) and Triplet (E_T) States, Activation Energies (E_{isc}) for the Intersystem Crossing Process, and Half-Wave Oxidation Potentials (E_{OX}) for Anthracene and Its Derivatives

compd	E_{S_1},[a] kJ mol^{-1}	E_{T_1}, kJ mol^{-1}	E_{isc}, kJ mol^{-1}	E_{T_2},[l] kJ mol^{-1}	E_{OX},[m] eV
anthracene	318	178[b]	4.6[h]	323	1.18
9-bromoanthracene	308	173[c]	12.1[i]	320	1.29
9-chloroanthracene	309		14.1,[h] 12.5[j]	322	
9-cyanoanthracene	299	169[d]	17.1[k]	316	1.57[f]
9-methylanthracene	310	173[b]	11.9[h]	322	0.96
9-methoxyanthracene	309		14.4[j]	323	1.05
9-phenylanthracene	312	176[d]	6.9,[i] 8.9[j]	320	1.13
9,10-dibromoanthracene	297	168[e]	18.7[i]	316	1.45
9,10-dichloroanthracene	298	169[e]	17.2,[h] 18.4[i]	316	
9,10-dicyanoanthracene	266	175[f]	24.9[k]	311	1.89[f]
9,10-diphenylanthracene	305	171[g]	13.5[k]	319	1.52
9,10-dimethylanthracene	301	168[d]	15.9[k]	317	1.67

[a] Determined from the position of the 0–0 band in the absorption spectra. [b] From ref 17. [c] From ref 22. [d] Measured in this work from $S_0 \rightarrow T_1$ oxygen enhanced absorption. [e] From ref 23. [f] From ref 3. [g] From ref 24. [h] From ref 25. [i] From ref 26. [j] Values measured in heptane, ref 27. [k] Calculated from correlation between E_{S_1} vs E_{isc} given in ref 26. [l] $E_{T_2} = E_{S_1} + E_{isc}$. [m] Versus SCE from ref 28 or ref 3 as indicated below.

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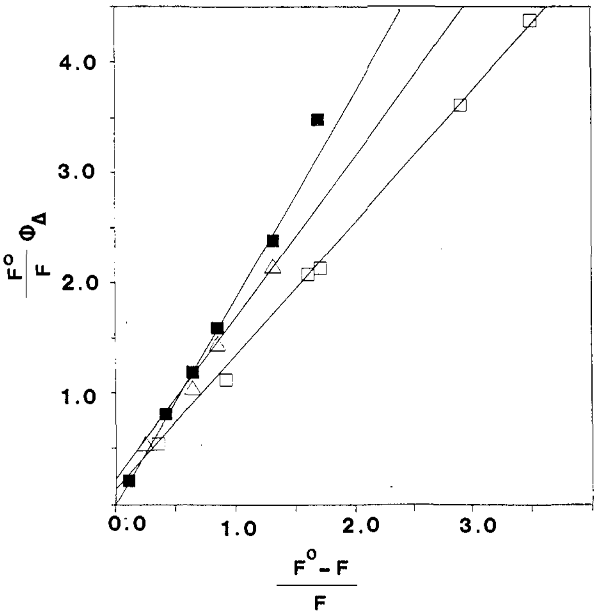

Figure 4. Plots to determine f_Δ^S and f_Δ^T according to eq 8: (■) 9,10-dicyanoanthracene, (△) 9-cyanoanthracene, and (□) 9,10-diphenylanthracene.

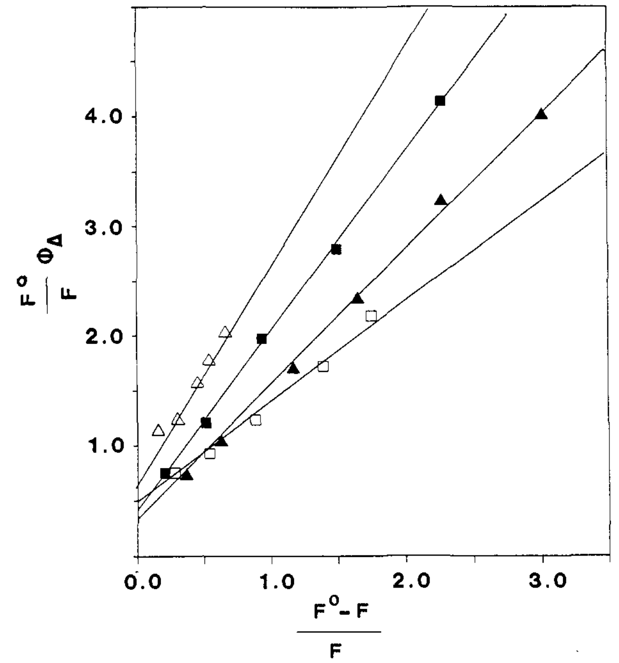

Figure 5. Plots to determine f_Δ^S and f_Δ^T according to eq 8: (■) 9,10-dichloroanthracene, (□) 9-phenylanthracene, (▲) 9-methoxyanthracene, and (△) 9,10-dibromoanthracene.

that the substituent shifts of the dimeso-substituted anthracenes are approximately twice those of the mono-substituted derivatives.

Plots according to eq 8 are shown in Figures 4–6 and the results are collected in Table II. The experimental errors (95% confidence limits) in the slopes of such plots, which equal ($f_\Delta^S + f_\Delta^T f_T^{O_2}$) are ≤±10%. However, the intercepts, which equal $\phi_T^O f_\Delta^T$, have errors of at least ±10% and are considerably higher in those cases such as 9,10-dicyanoanthracene where the intercept is close to zero. Literature values of triplet quantum yields are given in Table I and where possible those values which were not available were measured (e.g. see Figure 3). Values for ϕ_T^O combined with the intercepts to the plots shown in Figures 4–6 allow values of f_Δ^T to be determined. These f_Δ^T values are found to be unity within experimental error for all of the anthracene derivatives investigated. No value of ϕ_T^O is available for 9-chloroanthracene and therefore a value of $f_\Delta^T = 1$ is assumed in this case.

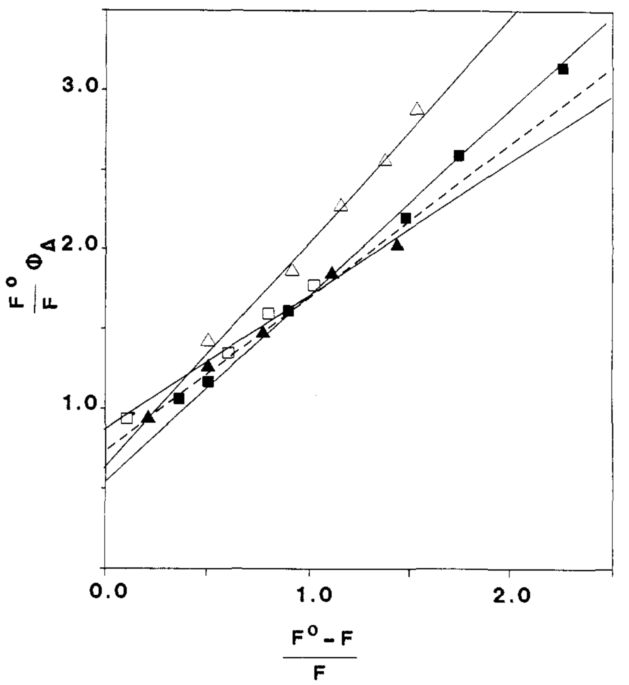

Figure 6. Plots to determine f_Δ^S and f_Δ^T according to eq 8: (△) 9-chloroanthracene, (□) 9-bromoanthracene, (■) 9-methylanthracene, and (▲) anthracene.

It is interesting to note that for those compounds with triplet yields in the range 0.26–0.71 where typical intercepts are obtained with 10–20% error, the values of $\phi_T^O f_\Delta^T$ are on average 10% higher than the values of ϕ_T^O. This may indicate that the standard value of ϕ_Δ of 0.92 used for *p*-methoxyacetophenone/naphthalene in cyclohexane with respect to which these values were measured may be 10% too high. However, Usui et al.,[6] who have measured ϕ_Δ, f_Δ^T, and f_Δ^S values in cyclohexane for three of the derivatives studied here by measuring quantum yields of photooxidation as a function of oxygen concentration, have obtained similar or slightly higher values in their work (see later). For those compounds such as 9-cyanoanthracene, 9,10-dicyanoanthracene, 9,10-diphenylanthracene, and 9,10-dimethylanthracene for which ϕ_T^O is less than 4%, we can only say from the intercepts that f_Δ^T are ≤1. This is of course consistent with these values also being one and there is no reason to assume that this is not the case. In fact in the case of 9,10-dicyanoanthracene one obtains the value $f_\Delta^T = 1$ from the slope of the plot according to eq 8, since the slope ($f_\Delta^S + f_\Delta^T f_T^{O_2}$) equals 2.1 ± 0.1 and this is only consistent with all three values, f_Δ^S, f_Δ^T, and $f_T^{O_2}$, being equal to 1. Other values for $f_T^{O_2}$, the fraction of singlet states quenched by oxygen which produce triplet states, were obtained using eq 14 for anthracene and 9-methyl-, 9-phenyl-, and 9,10-dichloroanthracene. The values obtained were 1.0 ± 0.1 (see Table II). It is interesting to note that Postashnik et al.[35] measured $f_T^{O_2} = 0.95$ and 0.9 for oxygen quenching of singlet anthracene in toluene and acetonitrile, respectively. They studied several hydrocarbons

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Table II. Singlet Oxygen Production from Singlet (f_Δ^S) and Triplet (f_Δ^T) States of Anthracene Derivatives in Cyclohexane,[a] Triplet Quantum Yields (ϕ_T), and the Fractions of Singlet States Quenched by Oxygen That Give Triplet States ($f_T^{O_2}$)

compd	$f_\Delta^S + f_\Delta^T f_T^{O_2}$	$\phi_T f_\Delta^T$	ϕ_T	f_Δ^T	f_Δ^S [k]	$f_T^{O_2}$
anthracene	0.91 ± 0.05	0.76 ± 0.05	0.71[b]	1.0 ± 0.1	0.0 ± 0.1	1.0 ± 0.1
9-bromoanthracene	0.96 ± 0.06	0.79 ± 0.04	0.70[c]	1.0 ± 0.1	0.0 ± 0.1	
9-chloroanthracene	1.41 ± 0.08	0.65 ± 0.07		(1.0)	(0.4)	
9-cyanoanthracene	1.51 ± 0.05	0.13 ± 0.04	0.04[d]	1.0	0.5 ± 0.1	
9-methylanthracene	1.12 ± 0.03	0.62 ± 0.05	0.63[b]	1.0 ± 0.1	0.1 ± 0.1	1.0 ± 0.1
9-methoxyanthracene	1.27 ± 0.03	0.25 ± 0.07	0.26[e]	1.0 ± 0.1	0.3 ± 0.1	
9-phenylanthracene	0.97 ± 0.06	0.42 ± 0.07	0.37[f]	1.0 ± 0.1	0.0 ± 0.1	1.0 ± 0.1
9,10-dibromoanthracene	1.76 ± 0.19	0.81 ± 0.08	0.70[g]	1.0 ± 0.1	0.8 ± 0.2	
9,10-dichloroanthracene	1.63 ± 0.03	0.36 ± 0.06	0.29[g]	1.0 ± 0.1	0.6 ± 0.1	1.0 ± 0.1
9,10-dicyanoanthracene	2.08 ± 0.10	0.0 ± 0.13	0.02[f]	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
9,10-diphenylanthracene	1.22 ± 0.02	0.06 ± 0.04	0.02[i]	1.0	0.2 ± 0.1	
9,10-dimethylanthracene	1.11 ± 0.02	0.07 ± 0.07	0.02[j]	1.0	0.1 ± 0.1	

[a] ϕ_Δ values were obtained relative to ϕ_Δ(p-methoxyacetophenone/naphthalene) = 0.92, ref 19. [b] Obtained by enhancement of intersystem crossing by xenon. [c] Unpublished result. [d] From ref 29. [e] Value measured in heptane, ref 27. [f] From ref 30. [g] Values measured in toluene, ref 31. [h] From ref 32. [i] From ref 33. [j] From ref 34. [k] For any assumptions made see text.

Table III. Rate Constants, $k_S^{O_2}$ and $k_T^{O_2}$, for Quenching of Singlet and of Triplet States, Respectively, of Anthracene Derivatives by Oxygen in Cyclohexane Solution

compd	$10^{-10}k_S^{O_2}$,[a] dm^3 mol^{-1} s^{-1}	$10^{-9}k_T^{O_2}$, dm^3 mol^{-1} s^{-1}	$k_T^{O_2}/k_S^{O_2}$	$k_T^{O_2}/k_{\mathrm{diff}}$[b]
anthracene	2.5	3.4	0.14	0.12
9-bromoanthracene	2.9	3.1	0.11	0.11
9-chloroanthracene	3.1	3.5	0.11	0.13
9-cyanoanthracene	0.67			
9-methylanthracene	3.0	3.3	0.11	0.12
9-methoxyanthracene	2.7	3.2	0.12	0.11
9-phenylanthracene	1.9	3.4	0.18	0.12
9,10-dibromoanthracene	2.4	2.7	0.11	0.10
9,10-dichloroanthracene	2.4	2.7	0.11	0.10
9,10-dicyanoanthracene	0.47			
9,10-diphenylanthracene	1.7			
9,10-dimethylanthracene	2.0	3.5	0.18	0.13

[a] From ref 39. [b] Using $k_{\mathrm{diff}} = 2.8 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, from ref 21.

and found $f_T^{O_2}$ close to one in toluene but often considerably less in acetonitrile. Where no value of $f_T^{O_2}$ has been determined it is assumed, in agreement with the measured values, that $f_T^{O_2} = 1$. This allows us to determine the f_Δ^S values and these are given in Table II. These values vary across the whole possible range from 0 to 1, in contrast to the values of f_Δ^T which are all unity.

Estimates of the errors given for f_Δ^S were arrived at as follows. For 9,10-dicyanoanthracene the slope of the plot shown in Figure 4 ($f_\Delta^S + f_\Delta^T f_T^{O_2} = 2.08 \pm 0.10$) is only consistent with all three fractions being equal to 1.0 ± 0.1. Since we have measured f_Δ^T and $f_T^{O_2}$ equal to unity for anthracene, 9-phenylanthracene, 9-methylanthracene, and 9,10-dibromoanthracene, f_Δ^S given in column 6 of Table II can be calculated without any further assumptions. In the case of 9-bromoanthracene, 9-methoxyanthracene, and 9,10-dibromoanthracene where we have shown that $f_\Delta^T = 1.0 \pm 0.1$, we have had to assume that $f_T^{O_2} = 1$ to obtain the values of $f_\Delta^S = 0.0 \pm 0.1$, 0.3, ± 0.1, and 0.8 ± 0.2, respectively. For 9-cyano-, 9,10-diphenyl-, and 9,10-dimethylanthracene for which ϕ_T^O values are less than 0.04, accurate values for f_Δ^T cannot be obtained from the intercepts of lines plotted according to eq 8. We have therefore for these three derivatives assumed both f_Δ^T and $f_T^{O_2}$ equal 1 to calculate the f_Δ^S values. We have made the same assumption in the case of 9-chloroanthracene since no value for ϕ_T^O is available for this derivative.

The fact that anthracene derivatives show no substitution effects on f_Δ^T contrasts with the situation for a series of naphthalene derivatives where even in cyclohexane values of f_Δ^T have been shown to be critically dependent on electron withdrawing and donating substituents.[36] The difference in behavior between anthracene and naphthalene derivatives is attributed to the location of the charge transfer states relative to the lowest triplet states in these two series of compounds. For naphthalene derivatives the charge transfer states are calculated to lie below the lowest locally excited triplet states for most derivatives,[11] whereas for the anthracene derivatives, they are calculated to be above. A good estimate for the energy of the charge transfer state of the complex between the hydrocarbons and oxygen is given by the Rehm–Weller equation[37]

$$E_{\mathrm{CT}} = F(E_{\mathrm{ox}}^{\mathrm{D}} - E_{\mathrm{red}}^{\mathrm{A}}) + \Delta\omega \qquad (15)$$

where $E_{\mathrm{ox}}^{\mathrm{D}}$ is the oxidation potential of the donor and $E_{\mathrm{red}}^{\mathrm{A}}$ is the reduction potential of the acceptor which has a value in the case of oxygen of −0.78 V versus SCE in acetonitrile.[38] The value of $\Delta\omega$ depends on Coulombic interactions and solvation energies and is difficult to calculate for encounter pairs, but it is likely to be constant for a series of related compounds. Knibbe, Rehm, and Weller[37c] have shown that $\Delta\omega = 0.15 \pm 0.1$ eV for the energy of 60 exciplexes which they studied in hexane.

The rate constants for oxygen quenching of the triplet states of the anthracene derivatives measured here are in the range 3.1 ± 0.4 × 10^9 dm^3 mol^{-1} s^{-1}. Again there is very little dependence of $k_T^{O_2}$ on substituents for anthracene derivatives in cyclohexane which contrasts with the situation for naphthalene derivatives where both $k_T^{O_2}$ and f_Δ^T vary substantially with substituents.[36] Since the quenching constants $k_S^{O_2}$ for 9-cyanoanthracene and 9,10-dicyanoanthracene are 6.7 and 4.7 × 10^9 dm^3 mol^{-1} s^{-1}, this clearly demonstrates that oxygen quenching of singlet states is not always diffusion controlled. Values of $k_T^{O_2}/k_S^{O_2}$ which vary from 0.11 to 0.18 are given in Table III. The values obtained for $k_T^{O_2}$ are all approximately equal to or slightly less than $^1/_9 k_{\mathrm{diff}}$ where $^1/_9$ is the spin statistical factor expected[14] for quenching by reaction 8, if one assumes that the diffusion controlled rate constant in cyclohexane (k_{diff}) is equal to 2.8 × 10^{10} dm^3 mol^{-1} s^{-1}, the average value calculated by Saltiel and Atwater[21] for $k_S^{O_2}$ for a set of aromatic hydrocarbons in cyclohexane (see Table III).

The efficiency of singlet oxygen production from the singlet state, f_Δ^S, varies from 0 to 1. In Figure 7 the zeroth-order energy levels of encounter complexes between anthracene and oxygen on the one hand and 9,10-dibromoanthracene and oxygen on the other are illustrated. In terms of the energy levels in this diagram, the fact that $f_\Delta^S = 0$ for anthracene suggests either a very fast decay through the triplet manifold, i.e., via the complex states labeled $^3(\mathrm{S}_1...^3\Sigma) \rightarrow {}^3(\mathrm{T}_2...^3\Sigma) \rightarrow {}^3(\mathrm{T}_1...^1\Delta) \rightarrow {}^3(\mathrm{T}_1...^3\Sigma)$, or

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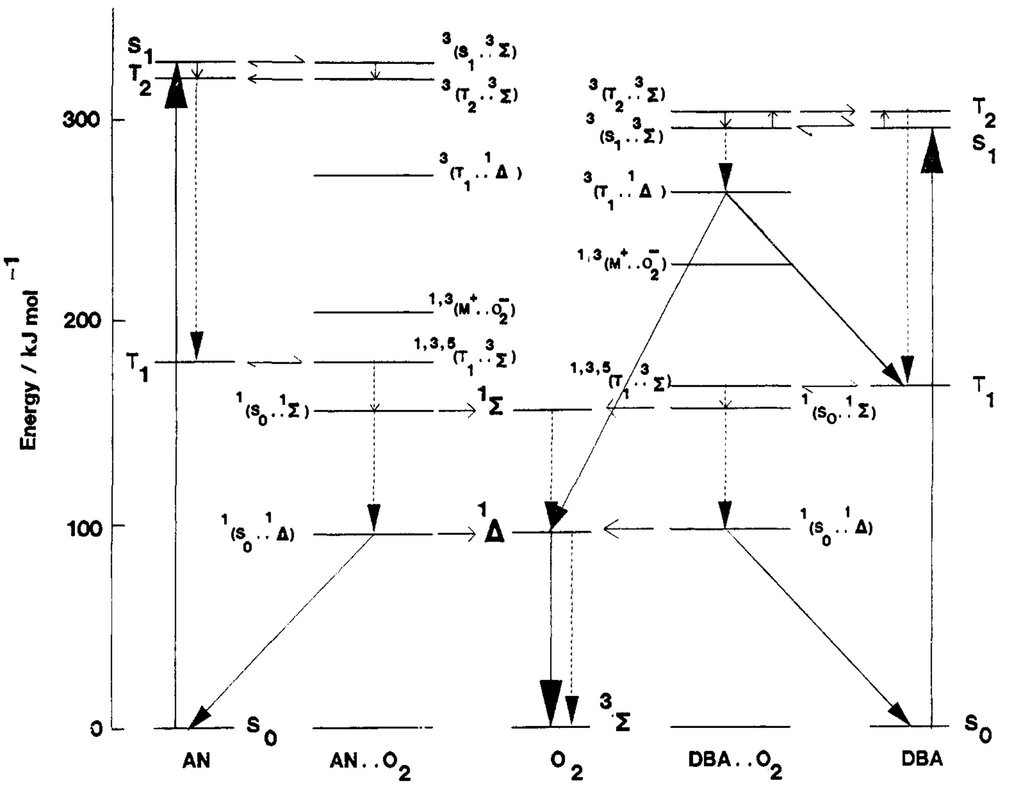

Figure 7. Schematic energy level diagram for anthracene (AN), 9,10-dibromoanthracene (DBA), molecular oxygen (O_2), and encounter complexes (AN...O_2 and DBA...O_2) illustrating major decay pathways.

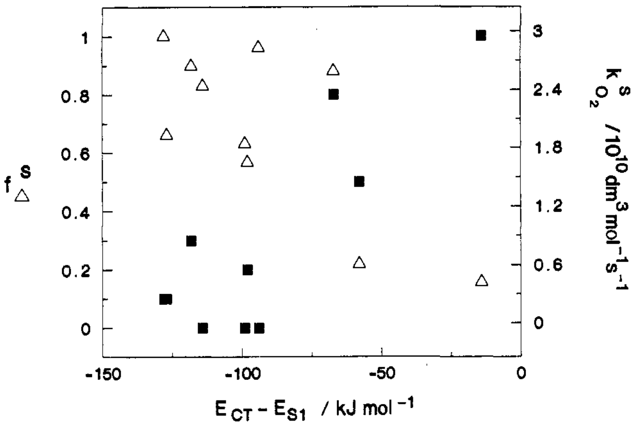

Figure 8. Plot of the fraction (f_Δ^S) of singlet oxygen produced due to oxygen quenching of the singlet state of anthracene derivatives (^{1}M) and of the oxygen quenching constants ($k_S^{O_2}$) against the difference in energy between the lowest singlet states and the ($M^+...O_2^-$) charge-transfer states ($E_{CT} - E_{S_1}$): (■) f_Δ^S and (△) $k_S^{O_2}$.

alternatively the complex labeled $^3(S_1...^3\Sigma)$ internally converts to the $^3(T_2...^3\Sigma)$ state which then dissociates to give T_2 and $O_2(^3\Sigma_g)$ with 100% efficiency. In other words the state labeled $^3(T_1...^1\Delta)$ either internally converts very rapidly or is not formed at all in the case of anthracene. If we consider the case of 9,10-dicyanoanthracene where $f_\Delta^S = 1$, this requires that the state labeled $^3(T_1...^1\Delta)$ is produced with unit efficiency and dissociates also with unit efficiency with no internal conversion to the lower $^3(T_1...^3\Sigma)$ state. Other anthracene derivatives, for example 9,10-dibromoanthracene (see Figure 7), lie between these two extremes, and the different efficiencies could be due to the varying involvement of charge transfer states. Figure 8 shows a plot of f_Δ^S against $\Delta E = E_{CT} - E_{S_1}$ calculated using E_{S_1} values given in Table I and eq 15 taking $\Delta\omega$ = 15 kJ mol^{-1} to calculate E_{CT}.[37b] Except in the case of 9,10-dicyanoanthracene, the charge transfer states are calculated to lie well below the S_1 state (58–128 kJ mol^{-1}, see also Figure 7), and internal conversion from the $(S_1...^3\Sigma)$ complex state therefore is probably much more likely to closely lying states such as $^3(T_2...^3\Sigma)$ or $^3(T_1...^1\Delta)$. Even indirect mixing between the S_1 and charge transfer states, which would be expected[14] to be inversely proportion to ΔE, is not apparent from the scatter of the data shown in Figure 8. In the case of 9,10-dicyanoanthracene, however, where ΔE is calculated to be −14 kJ mol^{-1}, i.e. the energy of the charge transfer state is calculated to be just below that of the S_1 state, it could be argued that the charge transfer assisted internal conversion to the $^3(T_1...^1\Delta)$ state is occurring since f_Δ^T is unity in this case. However, the low values of $k_S^{O_2}$ given in Table III show that 9,10-dicyanoanthracene and 9-cyanoanthracene have exceptionally low rate constants for quenching of their singlet states by oxygen which is not consistent with charge transfer assisted quenching. If anything there is an inverse relationship between $k_S^{O_2}$ and $E_{CT} - E_{S_1}$ as shown in Figure 8, but the data show considerable scatter. This demonstrates that in cyclohexane charge transfer interactions are not very significant in determining the efficiency of singlet oxygen production from excited singlet states of anthracene derivatives and we have already shown they do not affect f_Δ^T values. Other workers have shown that charge transfer interactions can be important in the oxygen induced deactivation of excited singlet states of organic molecules in acetonitrile,[3] i.e., when the solvent is polar. However as mentioned earlier, Postashnik et al.[35] have demonstrated that the oxygen catalyzed intersystem crossing efficiency ($f_T^{O_2}$) shows a marked dependence on solvent polarity.

As early as 1968, Stevens and Algar[34] attributed the relative unimportance of the spin allowed production of $O_2^*(^1\Delta_g)$ during oxygen quenching of singlet states of sensitizers in which the singlet–triplet splitting exceeds 94 kJ mol^{-1} to the formation of higher triplet state T_2. See also ref 40. More recently, Usiu et al.[6] have clearly demonstrated that the contribution to ϕ_Δ arising from singlet state quenching by oxygen depends markedly on the energy of T_2 states in certain compounds. Since $f_T^{O_2} = 1$ in all of the cases we have measured, it follows that $k_{S\Delta} + k_{ST} \gg k_{SO}$,

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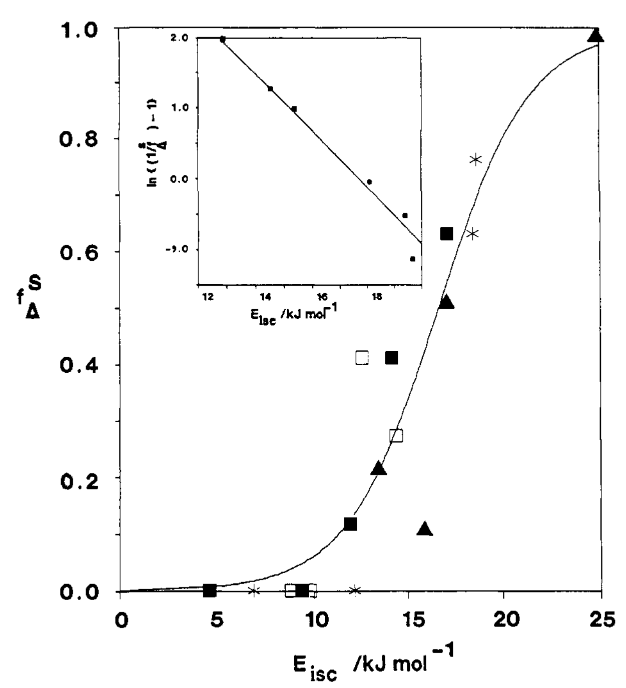

Figure 9. Plot of the fraction (f^S_Δ) of singlet oxygen produced due to oxygen quenching of the singlet state of anthracene derivatives versus the activation energy for intersystem crossing (E_{isc}), according to eq 13: (■) from ref 25, (*) from ref 26, (□) from ref 27, and (▲) extrapolated from the correlation given in ref 26. Insert shows a plot of $\ln\{(1/f^S_\Delta) - 1\}$ against E_{isc}.

and assuming this is the case for all of the anthracene derivatives, analysis of kinetic Scheme I gives

$$f^S_\Delta = \frac{k_4}{k_4 + k_5} = \frac{k_{S\Delta}}{k_{S\Delta} + k_{ST}} \qquad (16)$$

Examination of the energy diagram shown in Figure 7 reveals that reaction 4 must involve dissociation of the $^3(T_1...^1\Delta)$ state. Reaction 5 may involve dissociation of the $^3(T_2...^3\Sigma)$ state or internal conversion to the $^3(T_1...^3\Sigma)$ state. This latter process is ruled out at least for 9,10-dicyanoanthracene in cyclohexane because it does not explain the unit efficiency in this case. This leads us to suggest that the efficiency of production of singlet oxygen depends on competition between internal conversion either to the $^3(T_2...^3\Sigma)$ state or to the $^3(T_1...^1\Delta)$ state both of which dissociate efficiently. It has already been demonstrated[25-27] that intersystem crossings of many meso-substituted anthracene derivatives are temperature dependent with activation energies (E_{isc}) depending on the energy gap between their lowest excited singlet states (S_1) and higher triplet states. The activation energies for intersystem crossing measured from temperature dependence of fluorescence in the absence of oxygen are given in Table I. If f^S_Δ is reduced because of dissociation of the $^3(T_2...^3\Sigma)$ state to give the T_2 state of the hydrocarbon, lying at higher energy than the S_1 state, which then internally converts from the T_2 to the T_1 state without producing singlet oxygen, eq 16 becomes

$$f^S_\Delta = \frac{k_{S\Delta}}{k_{S\Delta} + Ae(-E_{isc}/RT)} \qquad (17)$$

for these meso-substituted anthracenes. Equation 17 rearranges to give

$$\frac{1}{f^S_\Delta} - 1 = \frac{Ae(-E_{isc}/RT)}{k_{S\Delta}} \qquad (18)$$

in which case a plot of $\ln\{1/f^S_\Delta - 1\}$ versus E_{isc} should be linear with a slope of $-1/RT$. Such a plot is shown as an insert in Figure 9, and the linear part of this curve has a slope of -0.41 mol kJ^{-1}, which agrees very well with the expectation value for $1/RT$. Figure 9 shows a plot of f^S_Δ versus E_{isc} according to eq 17 which clearly demonstrates that f^S_Δ increases with increasing E_{isc} and thus quenching of singlet excited states of anthracene derivatives by molecular oxygen therefore involves efficient dissociation from both $^3(T_2...^3\Sigma)$ and $^3(T_1...^1\Delta)$ states when they are formed and the efficiency of singlet oxygen production depends almost completely upon the extent to which these two states are formed.

As mentioned earlier, Usui et al.[6] have recently evaluated f^S_Δ and f^T_Δ values for anthracene, 9,10-dimethylanthracene, and 9,10-dicyanoanthracene in cyclohexane from fluorescence quenching measurements coupled with measurements of the quantum yields of photosensitized oxidation of 1,3-diphenylisobenzofuran as a function of oxygen concentration. These workers assumed $f^{O_2}_T = 1$ and measurements given in this paper would support this assumption. Our values for f^T_Δ which all equal 1 are in agreement with their values. However, our values for f^S_Δ for anthracene and 9,10-dimethylanthracene of 0 and 0.11 respectively do not compare so favorably with their values of 0.3 and 0.2, respectively. In the case of 9,10-dicyanoanthracene our values of $f^S_\Delta = 1$ and $f^S_\Delta + f^{O_2}_T f^T_\Delta = 2.1 \pm 0.1$ agree very well with those of Usui et al.[6] Only in the case of anthracene in cyclohexane is the discrepancy beyond the expected experimental errors. The only other measurement on anthracene derivatives in cyclohexane as solvent which is relevant to this work is the value obtained by Kristiansen et al.[4] for 9,10-dicyanoanthracene in cyclohexane of $f^S_\Delta + f^{O_2}_T f^T_\Delta = 1.9$ obtained as a limiting value at infinite oxygen concentration. This is in good agreement with our value and that of Usui et al.[6] Bearing in mind the dangers of comparing values for singlet oxygen formation efficiencies in different solvents, we feel that it is pertinent to mention that Wu and Trozzolo[15] found the following values for f^S_Δ in *n*-hexane from studies of the sensitized photooxidation of 2,5-dimethylfuran coupled with fluorescence quenching measurements. These authors found $f^S_\Delta \geq 0.19$, 0.42, 0.41, and 0.48 for 9-methyl-, 9-phenyl-, 9,10-dimethyl-, and 9,10-diphenylanthracene, respectively. Our values in cyclohexane for these same compounds, given in Table II, are 0.1, 0.0, 0.1, and 0.2 for 9-methyl-, 9-phenyl-, 9,10-dimethyl-, and 9,10-diphenylanthracene. Once again it is apparent that the values we have obtained from emission measurements are lower than those obtained using measurements of quantum yields of photooxidation but the different solvent has to be borne in mind. The only other value which has been measured for f^S_Δ of anthracene is that by Stevens et al.,[16] who also use photosensitized oxidation measurements and found $f^S_\Delta = 0.46$ for anthracene in benzene solution. It is worth noting that some photooxidation quantum yields of furans are anomalously high because of the destruction of furans by intermediate endoperoxides[41] which may account for some of the differences between the values presented here and those given in refs 6, 15, and 16. We are currently investigating the influence of the solvent on f^T_Δ and f^S_Δ and since this is considerable, further work is needed before critical evaluation of available data can be made.

Conclusion

Measurements of the yields of singlet oxygen production combined with fluorescence quenching measurements for anthracene and eleven of its meso derivatives have clearly demonstrated that the fraction of triplet states quenched by oxygen which yield $O_2^*(^1\Delta_g)$ is unity in all cases. We have shown that the fraction of triplet states produced following oxygen quenching of singlet states of anthracene and 9-phenyl-, 9,10-dichloro-, and 9,10-dicyanoanthracene in cyclohexane is also unity. However, the fraction of quenching of the excited singlet states of these derivatives by oxygen which yield $O_2^*(^1\Delta_g)$, f^S_Δ, is only unity in the case of 9,10-dicyanoanthracene. Values of f^S_Δ, which vary in

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cyclohexane from zero in the case of anthracene, 9-bromoanthracene, and 9-phenylanthracene to one in the case of 9,10-dicyanoanthracene, have been shown to depend on the efficiency of formation of the triplet encounter complex $^3(T_2...^3\Sigma)$, which dissociates to give ground state oxygen and the T_2 state of the separated anthracene derivative, which then dissipates excess energy by internally converting to its T_1 state, without forming singlet oxygen. The efficiency of formation of this $^3(T_2...^3\Sigma)$ state is often temperature dependent for meso derivatives of anthracene and this is shown to determine the value of f_Δ^{δ} with dissociation of $^3(T_2...^3\Sigma)$ states being much more likely than internal conversion to the lower complex state, $^3(T_1...^1\Delta)$, dissociation of which produces singlet oxygen. These processes are both temperature and solvent dependent and consequently a considerably amount of work remains to be done before it is possible to provide a complete description of the interactions between molecular oxygen and the excited state of anthracene derivatives.

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