

## Quenching of Excited States of Aromatic Hydrocarbons and their Derivatives by Oxygen

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Medidas dos rendimentos de produção de oxigênio singlete combinados com medidas de supressão de fluorescência permitem a avaliação das eficiências de produção de oxigênio singlete a partir dos estados singlete e triplete de uma série de derivados de antraceno em ciclohexano e acetonitrila. A eficiência de produção de oxigênio singlete a partir de estados triplete de antraceno e alguns de seus meso-derivados,  $f_{\Delta}^T$  é unitário, com a exceção de 9-metoxiantraceno em acetonitrila, onde o valor cai para um terço.  $f_{\Delta}^T$  também foi medido para um conjunto de naftalenos substituídos em acetonitrila, benzeno e ciclohexano. É demonstrado que o  $f_{\Delta}^T$  para os derivados de naftaleno apresenta grande sensibilidade ao potencial de oxidação dos compostos, com valores variando entre 0.33 e a unidade. As constantes de velocidade bimoleculares para a supressão dos estados triplete dos derivados de naftaleno por oxigênio,  $k_T^{O_2}$  correlacionam inversamente com  $f_{\Delta}^T$ . Foi encontrado que tanto o  $k_T^{O_2}$  quanto  $f_{\Delta}^T$  dependem fortemente com  $\Delta G^{CT}$ , a variação de energia livre para a formação do estado de transferência de carga do estado triplete, o que mostra a importância da participação das interações de transferência de carga durante a supressão. A diferença entre o comportamento de antracenos e naftalenos substituídos por ser atribuída ao fato de que a energia do estado de transferência de carga do complexo de encontro entre o oxigênio e o hidrocarboneto subsequente à transferência de elétron do hidrocarboneto ao  $O_2$ , é maior que a do menor estado triplete localmente excitado para todos os derivados de antraceno, exceto para 9-metoxiantraceno em acetonitrila. Por outro lado, aquele estado é menor para a maior parte dos derivados de naftaleno. Mostra-se que para os derivados de antraceno a eficiência de produção de oxigênio singlete a partir de estados singlete suprimidos por oxigênio,  $f_{\Delta}^S$ , e a fração de estados singlete suprimidos por oxigênio que dão estados tripletes,  $f_T^{O_2}$  são menores no solvente polar, acetonitrila, que em ciclohexano. Isto sugere que as interações de transferência de carga podem também ser responsáveis pela redução nos rendimentos de oxigênio singlete observados para os derivados de antraceno no solvente mais polar.

Measurements of the yields of singlet oxygen production combined with the fluorescence quenching measurements allows the efficiency of singlet oxygen production from singlet and triplet states of a series of anthracene derivatives to be measured in cyclohexane and acetonitrile. For anthracene and several of its meso-derivatives, the efficiency of singlet oxygen production from triplet states quenched by oxygen  $f_{\Delta}^T$  is found to be unity with the exception of 9-methoxyanthracene in acetonitrile where the value drops to one third.  $f_{\Delta}^T$  was also measured for a range of substituted naphthalenes in acetonitrile, benzene and cyclohexane. For naphthalene derivatives  $f_{\Delta}^T$  is shown to exhibit a pronounced sensitivity to the oxidation potential of the compound with values varying from 0.33 to unity. The bimolecular rate constants for oxygen quenching of the triplet state of these naphthalene derivatives,  $k_T^{O_2}$  correlates inversely with  $f_{\Delta}^T$ . Both  $k_T^{O_2}$  and  $f_{\Delta}^T$  are shown to be strongly dependent on  $\Delta G^{CT}$ , the free energy change for charge transfer state formation from the triplet state which demonstrates the importance of the participation of charge transfer interactions during quenching. The difference in behavior between substituted anthracenes and naphthalenes can be ascribed to the fact that the energy of the charge transfer state of the encounter complex between oxygen and the hydrocarbon produced following electron transfer from the hydrocarbon to  $O_2$  is higher than the lowest locally excited triplet state in the case of all the anthracene derivatives, with the exception of 9-methoxyanthracene in acetonitrile, but lower in the case of most of the naphthalene derivatives. For anthracene derivatives  $f_{\Delta}^S$ , the efficiency of singlet oxygen production from

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singlet states quenched by oxygen and  $f_T^{O_2}$ , the fraction of singlet states quenched by oxygen which give triplet states, are shown to be less in the polar solvent, acetonitrile, than in cyclohexane. This suggests that charge transfer interactions may also be responsible for the reduction in the yields of singlet oxygen observed for anthracene derivatives in the more polar solvent.

**Keywords:** oxygen quenching, singlet oxygen, excited states, aromatic hydrocarbons

## Introduction

Oxygen quenching of electronically excited states is a very well known phenomena. However misconceptions concerning quenching by oxygen are widespread, for example it is often claimed: (i) that oxygen quenching of excited singlet states is always diffusion controlled, (ii) that the rate constants for oxygen quenching of triple states reaches a maximum value of one ninth of diffusion controlled due to the spin statistical factor for the formation of the singlet encounter complex being one ninth, (iii) the efficiency of formation of singlet oxygen during oxygen quenching of triplet states is unity, (iv) that oxygen quenching of triplet states but not singlet states produces singlet oxygen  $O_2^*(^1\Delta_g)$ , (v) that oxygen quenching of excited singlet states yields triplet states by catalyzed intersystem crossing invariably with unit efficiency, and (vi) that oxygen quenching shows little dependence, on the nature of the excited state being quenched. Recent and earlier studies<sup>1-21</sup> demonstrate that none of the statements (i)-(vi) hold universally and the number of exceptions is considerable. There has been much recent interest in factors which determine oxygen quenching of excited states and the efficiency of formation thereby of single oxygen. It is becoming 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<sup>1-21</sup>.

In this paper we report the measurement of  $f_{\Delta}^S$  and  $f_{\Delta}^T$ , the efficiencies of singlet oxygen production from excited singlet states and from triplet states quenched by oxygen respectively and  $f_T^{O_2}$ , the fraction of singlet states quenched by oxygen which yield triplet states. We use these measurements and other examples mainly from our recent work to clearly demonstrate that there are many exceptions to (i)-(vi) above. The reasons for the different behavior of different molecules are discussed.

## Experimental

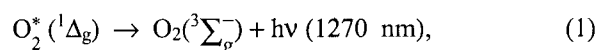
### Materials

Anthracene, and 9,10-diphenylanthracene, (Aldrich) were used as received; 9-phenylanthracene, Acridine (Aldrich) and 9,10-dichloroanthracene, 9-methylanthracene, (Eastman Kodak) were recrystallised from ethanol; 9,10-dibromoanthracene, 9-cyanoanthracene

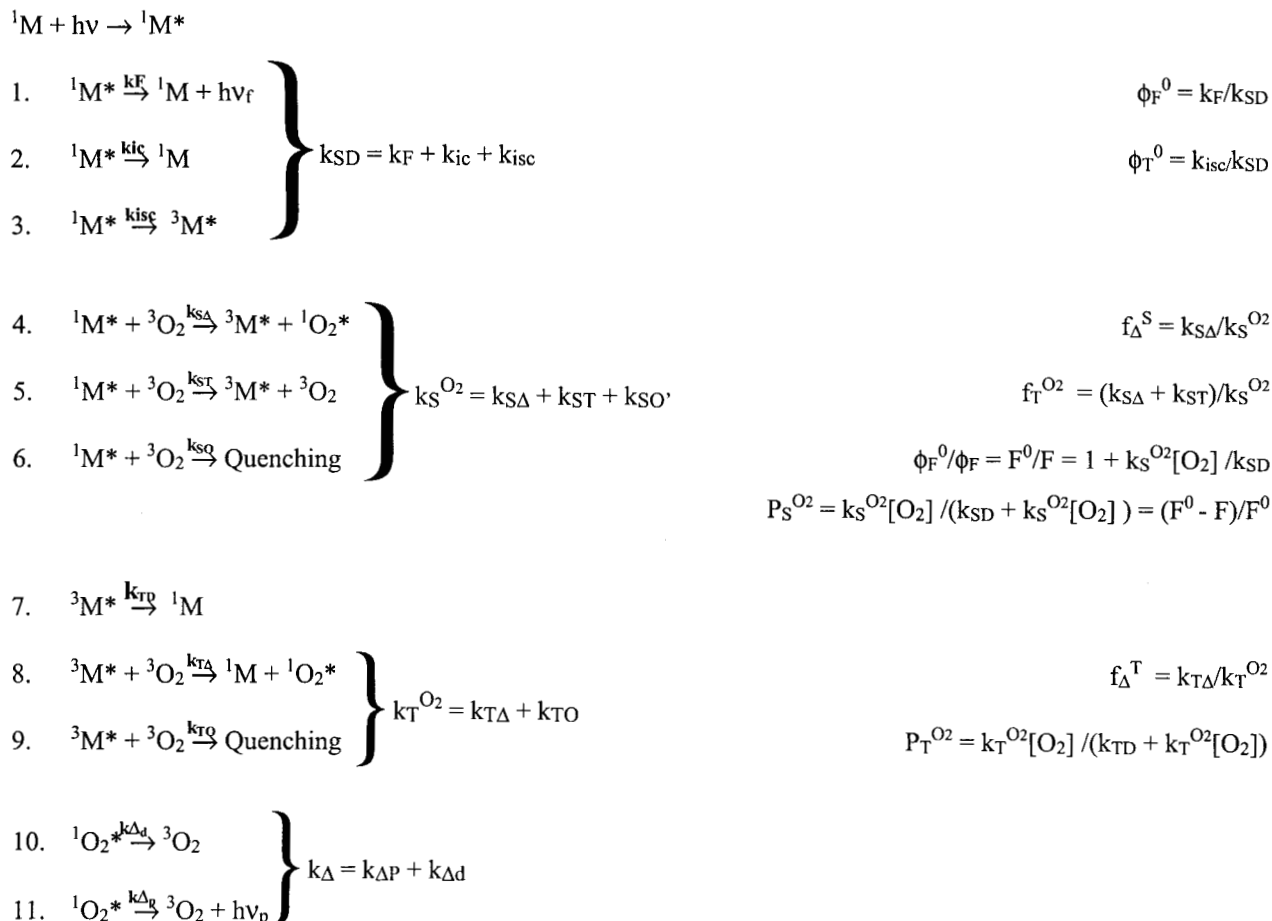
(Aldrich) and 9,10-dicyanoanthracene (Kodak) were recrystallised from benzene. Phenazine (Pz), 2-bromonaphthalene and 2-methoxynaphthalene (Aldrich) were recrystallised from ethanol; biphenyl (Aldrich, 99%) was sublimed; 1-methylnaphthalene, 1-methoxynaphthalene and 1-bromonaphthalene were purified by repeated vacuum distillation; naphthalene (N) (Aldrich scintillation grade, Gold Label), 1-ethylnaphthalene (Fluka, 99%), benzophenone (BP) (Aldrich, Gold Label) and p-methoxyacetophenone (pMAP) (Aldrich, 99%) were used as received; acenaphthene, 2-methylnaphthalene, 2-ethylnaphthalene, 1-fluoronaphthalene, 1-chloronaphthalene and 1-cyanoanthracene (Aldrich) were used as received; 9-methoxyanthracene was a gift from the late E. J. Bowen and was recrystallised from ethanol, tetraphenylporphyrin (TPP) was a gift from C. Tanielian, Strasbourg, France. Acetonitrile (Aldrich, spectrophotometric grade) was dried by refluxing over calcium hydride; benzene (Aldrich spectrophotometric grade) and cyclohexane (Aldrich spectrophotometric and anhydrous grades) were used as received.

### Apparatus

Absorption spectra were recorded with a Phillips PU8800 Spectrophotometer. Fluorescence measurements were carried out using a Perkin Elmer LS4 Spectrofluorimeter. Transient absorption spectra were obtained using a nanosecond laser flash photolysis system with right angle geometry as described elsewhere<sup>21</sup>. Excitation was with 8 ns pulses at 355 nm obtained from a frequency tripled Lumonics HY200 Q-switched neodymium-YAG laser. Singlet oxygen was detected by monitoring the 0,0 vibronic band of the phosphorescence centred at 1270 nm,



using a Judson germanium photodiode (J16-8SP-RO5M, active diameter is 0.5 cm) coupled to a Judson PA100 amplifier. The phosphorescence was detected at right angles to the exciting beam through a silicon cutoff filter. The laser energies employed did not exceed 0.7 mJ pulse<sup>-1</sup>. Individual luminescence traces were signal-averaged and fitted using a single exponential function to yield the luminescence intensity  $I_0$  at  $t = 0$ . The  $I_0$  values were plotted against relative laser intensity to obtain plots which were



### Scheme 1.

linear below 0.5 mJ pulse<sup>-1</sup>. Comparison of the slopes of these plots give relative singlet oxygen yields<sup>20</sup>.

### Method

The mechanism by which oxygen quenches the excited states of a hydrocarbon, M, excited to singlet and triplet states <sup>1</sup>M\* and <sup>3</sup>M\* respectively is shown in Scheme 1 where the symbols used for the rate constants, quantum yields and fractional formation efficiencies are also defined. The quantum yield of sensitized production of singlet oxygen,  $\phi_{\Delta}$ , is given by the sum of the contributions arising from oxygen quenching of the lowest excited singlet state (S<sub>1</sub>) and the lowest excited triplet state (T<sub>1</sub>) of the sensitizer, *i.e.*:

$$\phi_{\Delta} = \phi_{\Delta}(S_1) + \phi_{\Delta}(T_1) \quad (2)$$

This can be written in terms of  $f_{\Delta}^S$  and  $f_{\Delta}^T$ , defined in Scheme 1 as

$$\phi_{\Delta} = f_{\Delta}^S P_{S^{O_2}} + \phi_T^{O_2} f_{\Delta}^T P_{T^{O_2}} \quad (3)$$

where  $P_{S^{O_2}}$  and  $P_{T^{O_2}}$  equal the fraction of singlet and triplet states respectively which are quenched by oxygen and  $\phi_T^{O_2}$

is the quantum yield of triplet state production in the presence of oxygen.

It follows from Scheme 1 that  $\phi_T^{O_2}$  is given by

$$\phi_T^{O_2} = \phi_T^0 (1 - P_{S^{O_2}}) + f_T^{O_2} P_{S^{O_2}} \quad (4)$$

where  $f_T^{O_2}$  is the fraction of singlet states quenched by oxygen which yield triplet states.

### Measurement of Oxygen Quenching Rate Constants ( $k_T^{O_2}$ )

The rate constants ( $k_T^{O_2}$ ) for oxygen quenching of the triplet states were determined by kinetic absorption measurements on air-equilibrated solutions. The intrinsic first-order triplet decay rate constant ( $k_1$ ) is small compared with the pseudo first-order oxygen quenching rate constant ( $k_2 = k_T^{O_2}[O_2]$ ) for the molecules studied and so decay of the triplet states in the presence of oxygen by routes other than by oxygen quenching may be neglected. Ten single-shot kinetic absorption traces were signal-averaged for each measurement and excellent single-exponential fits were obtained for all the triplet state decays in air-equilibrated solvents. The oxygen concentrations in air-equilibrated solvents were taken to be  $1.9 \times 10^{-3}$  mol dm<sup>-3</sup> in acetonitrile,

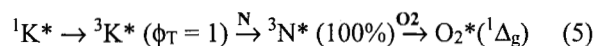
$1.9 \times 10^{-3} \text{ mol dm}^{-3}$  in benzene and  $2.4 \times 10^{-3} \text{ mol dm}^{-3}$  in cyclohexane<sup>22</sup>.

*Measurements of singlet oxygen formation efficiencies ( $\phi_{\Delta}$ )*

*(a)  $\phi_{\Delta}$  measured with sensitized triplet production*

The procedure for the determination of singlet oxygen yields following sensitized production of triplet states was as follows. Air-equilibrated solutions of the substituted naphthalenes ( $0.05\text{--}0.1 \text{ mol dm}^{-3}$ ) each containing an aromatic ketone sensitizer, were optically matched ( $\pm 0.01$  absorbance units) at the laser excitation wavelength to a standard reference solution for which the singlet oxygen yield is known. Solutions were prepared in 1 cm square quartz cells with absorbances at 355 nm of  $\sim 0.5$ . This procedure eliminates the requirement to apply corrections for different fractional absorption of the exciting light. The concentrations of the substituted naphthalenes in these solutions are not high enough to significantly influence the refractive index of the solvent and therefore it was not necessary to apply any refractive index correction factor<sup>4</sup>.

The use of aromatic ketones as sensitizers for the substituted naphthalene triplet states has been used previously by ourselves<sup>23</sup> and by Gorman *et al.*<sup>24</sup> to allow the production of the naphthalene (N) triplet state with unit efficiency by energy transfer from the aromatic ketone (K) triplet state, viz.,



Since the singlet oxygen yield ( $\phi_{\Delta}$ ) arises only from oxygen quenching of triplet states Eq. 3 simplifies to give

$$\phi_{\Delta} = \phi_{\text{T}} f_{\Delta}^{\text{T}} P_{\text{T}}^{\text{O}_2} \quad (6)$$

where  $\phi_{\text{T}}$  is the quantum yield of triplet state production under the conditions of the experiment and  $P_{\text{T}}^{\text{O}_2}$  is the fraction of triplet states quenched by oxygen. For all naphthalene derivatives, which were sensitized using aromatic ketones, we assume energy transfer from the triplet ketone to be 100% efficient. Support for this assertion is given in Refs. 25 and 26. Since triplet energy transfer gives  $\phi_{\text{T}} = 1$  and since for all the naphthalene derivatives studied here  $P_{\text{T}}^{\text{O}_2} = 1$ , it follows that in these experiments  $\phi_{\Delta} = f_{\Delta}^{\text{T}}$ .

In the determination of  $f_{\Delta}^{\text{T}}$  values the time resolved 1270 nm luminescence signal was recorded following 355 nm laser excitation of each solution at variable laser intensities. At each laser intensity the recorded luminescence trace was obtained by signal averaging ten single shot traces. For each solution the averaged luminescence traces at different laser intensities were fitted using a single exponential function in order to extract the initial luminescence intensity ( $I_0$ ) at time  $t = 0$ . Plots of  $I_0$  vs. laser intensity

were observed to be linear up to incident laser intensities of  $0.5 \text{ mJ pulse}^{-1}$ . Within this laser intensity range 15–20 data points were obtained for each plot. The slopes of the  $I_0$  vs. laser intensity plots are proportional to  $f_{\Delta}^{\text{T}}$  and thus  $f_{\Delta}^{\text{T}}$  values may be obtained by comparison with the slope obtained for the reference standard. For each compound at least three separate determinations of  $f_{\Delta}^{\text{T}}$  were carried out. The mean singlet oxygen lifetimes ( $\tau_{\Delta}$ ) of  $80 \mu\text{s}$  in acetonitrile,  $31 \mu\text{s}$  in benzene, and  $24 \mu\text{s}$  in cyclohexane, which we observed are in good agreement with previous measurements in the literature<sup>4,27</sup>. The standards which we have employed are as follows: (a) acetonitrile: acridine in air-equilibrated acetonitrile for which  $\phi_{\Delta} = 0.82$ <sup>28</sup>, (b) benzene: naphthalene ( $0.1 \text{ mol dm}^{-3}$ ) in air-equilibrated benzene containing benzophenone for which  $\phi_{\Delta} = f_{\Delta}^{\text{T}}(\text{N}) = 0.62$ <sup>10,11</sup>, and (c) cyclohexane: naphthalene ( $0.1 \text{ mol dm}^{-3}$ ) in air-equilibrated cyclohexane containing *p*-methoxyacetophenone for which  $\phi_{\Delta} = f_{\Delta}^{\text{T}}(\text{N}) = 0.92$ <sup>19</sup>.

*(b)  $\phi_{\Delta}$  measured when both singlet and triplet states are quenched by oxygen*

According to the kinetic mechanism depicted in Scheme 1, when  $P_{\text{T}}^{\text{O}_2} = 1$ , *i.e.* when  $k_{\text{T}}^{\text{O}_2}[\text{O}_2] \gg k_{\text{T}\text{D}}$  the singlet oxygen quantum yield,  $\phi_{\Delta}$ , and the fluorescence intensities in the presence and absence of oxygen,  $F$  and  $F^0$ , are related through the following equation<sup>10</sup>,

$$\phi_{\Delta} \frac{F^0}{F} = (f_{\Delta}^{\text{S}} + f_{\text{T}}^{\text{O}_2} f_{\Delta}^{\text{T}}) \left[ \frac{F^0}{F} - 1 \right] + \phi_{\text{T}}^{\text{O}} f_{\Delta}^{\text{T}} \quad (7)$$

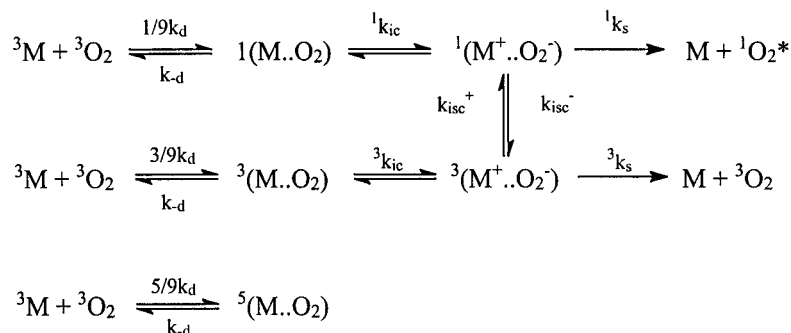
$\phi_{\Delta}$  measurements were combined with fluorescence intensity measurements at different oxygen concentrations to evaluate  $f_{\Delta}^{\text{T}}$  and  $(f_{\Delta}^{\text{S}} + f_{\text{T}}^{\text{O}_2} f_{\Delta}^{\text{T}})$ , from plots based on Eq. 7. For each anthracene derivative six different concentrations of oxygen were used and for each of these solutions the relative steady state fluorescence intensity was measured.

*Measurement of the fraction of singlet states quenched by oxygen which yield triplet states ( $f_{\text{T}}^{\text{O}_2}$ )*

From the ratio of the triplet absorbances at time  $t = 0$  in the presence and absence of oxygen, values of  $f_{\text{T}}^{\text{O}_2}$  were measured using the following equation which can easily be derived from the reaction mechanism given in Scheme 1, see also Ref. 29.

$$f_{\text{T}}^{\text{O}_2} = \frac{\phi_{\text{T}}^{\text{O}} \left( \frac{A_{\text{T}}^{\text{O}_2}}{A_{\text{T}}^{\text{O}}} - \frac{F}{F^0} \right)}{\left( 1 - \frac{F}{F^0} \right)} \quad (8)$$

where  $A_{\text{T}}^{\text{O}_2}$  and  $A_{\text{T}}^{\text{O}}$  are the triplet absorbances in the presence and absence of air, which are directly proportional to  $\phi_{\text{T}}^{\text{O}_2}$  and  $\phi_{\text{T}}^{\text{O}}$  respectively.



Scheme 2.

## Results and Discussion

In order to discuss the results obtained for  $k_T^{O_2}$  and  $f_{\Delta}^T$  we need to consider Reactions 8 and 9 in Scheme 1 in more detail as shown in Scheme 2 which one of us proposed in 1977. This scheme includes the involvement of charge transfer (CT) states to explain the high oxygen quenching rate constants, with  $k_T^{O_2}$  greater than  $k_{diff}/9$ , observed for oxygen quenching of the triplet states of certain aromatic ketones and amines<sup>30</sup>. It was suggested that as a consequence of intersystem crossing between CT states the observed singlet oxygen yield should be in the range 0.25 - 1.0.

Recent investigations<sup>7,16</sup> on the quenching of triplet states by oxygen at low temperature have indicated a maximum limiting value of  $4/9 k_{diff}$ , for  $k_T^{O_2}$  even with  $f_{\Delta}^T$  close to unity. This requires intersystem crossing as shown in the above scheme. However a recent study by Hirayama *et al.*<sup>31</sup> indicates that at high pressures up to 400 MPa for 9-methylanthracene in 2,2,4,4,6,8,8 heptamethylnonane, where the viscosity is increased up to  $10^7$  cP the value of the ratio  $k_T^{O_2}/k_S^{O_2}$  is 0.9 and with increasing viscosity appears to be approaching unity. This suggests that at least in very viscous solvents, intersystem crossing from the quintet state of the encounter complex can occur. There is as yet little evidence which demonstrates the importance of the quintet state of the encounter complex under more normal conditions.

Table 1 gives for the various naphthalene derivatives, the triplet energies ( $E_T$ ), the half wave oxidation potentials ( $E_M^{OX}$ ), and the free energy changes  $\Delta G^{CT}$  for ion pair formation from their triplet states calculated from the Rehm Weller equation<sup>32</sup>

$$\Delta G^{CT} = F [ E_M^{OX} - E_{O_2}^{red} ] - E_T \quad (9)$$

where  $F$  is the Faraday constant and  $E_{O_2}^{red}$  is the half-wave reduction potential for  $O_2(^3\Sigma_g^-)$ , taken to be  $-0.78$  V vs. SCE<sup>33</sup>. The measured values for naphthalene derivatives of  $f_{\Delta}^T$  and  $k_T^{O_2}$  in acetonitrile, benzene and cyclohexane are given in Tables 1 and 2 respectively.

The photophysical properties of anthracene and several of its derivatives are collected in Table 3 together with the rate constants for quenching of singlet and triplet states respectively of anthracene derivatives by oxygen in cyclohexane solution. Quenching constants  $k_S^{O_2}$  for 9-cyanoanthracene and 9,10-dicyano-anthracene in cyclohexane<sup>35</sup> are  $6.7$  and  $4.7 \times 10^9$   $dm^3 mol^{-1} s^{-1}$ , which clearly illustrates that oxygen quenching of singlet states is not always diffusion controlled (see also Ref. 31). The diffusion controlled rate constant in cyclohexane ( $k_{diff}$ ) can be taken equal to  $2.8 \times 10^{10}$   $dm^3 mol^{-1} s^{-1}$ , the average value calculated by Saltiel and Atwater<sup>36</sup> for  $k_S^{O_2}$  for a set of aromatic hydrocarbons in cyclohexane. The rate constants for oxygen quenching in cyclohexane of the triplet states of the anthracene derivatives measured are in the range  $3.1 \pm 0.4 \times 10^9$   $dm^3 mol^{-1} s^{-1}$  and although these values of  $k_T^{O_2}$  are all close to, or slightly less than  $k_{diff}/9$  where  $1/9$  is the spin statistical factor expected for quenching by Reaction 8, this contrasts with the situation for naphthalene derivatives shown in Table 2 where  $k_T^{O_2}$  values in cyclohexane and in the other two solvents are sensitive to the oxidation potential of the naphthalene derivative. The diffusion controlled rate constant in acetonitrile and benzene for oxygen quenching ( $k_{diff}$ ) can be taken equal to  $3.7 \times 10^{10}$   $dm^3 mol^{-1} s^{-1}$  and  $3 \times 10^{10}$   $dm^3 mol^{-1} s^{-1}$  respectively<sup>37</sup>. In the case of the methoxynaphthalene derivatives and acenaphthalene in acetonitrile and benzene the values of  $k_T^{O_2}$  are considerably greater than  $k_{diff}/9$ .

From Tables 1 and 2 it is apparent that for naphthalene derivatives in all three solvents  $k_T^{O_2}$  exhibits an inverse dependence on  $\Delta G^{CT}$ . It is also clear from Tables 1 and 2 that  $f_{\Delta}^T$  varies with  $\Delta G^{CT}$  in the opposite manner to  $k_T^{O_2}$  and that  $f_{\Delta}^T$  and  $k_T^{O_2}$  are inversely correlated. In order to estimate  $\Delta G^{CT}$  from Eq. 9 with cyclohexane as solvent it is necessary to include an additional term  $\Delta\omega$  which depends on coulombic interactions and solvation energies. The magnitude of  $\Delta\omega$  for encounter pairs is difficult to calculate but it is likely to be constant for a series of structurally similar compounds. Knibbe, Rehm and Weller<sup>32</sup> have

**Table 1.** The efficiency of production of singlet oxygen during quenching of triplet states of naphthalene derivatives by oxygen  $f_{\Delta}^T$  in acetonitrile (A), benzene (B) and cyclohexane (C).

Sensitizer	$E_T^{(a)}$ kJ mol <sup>-1</sup>	$E_M^{OX(b)}$ V	$\Delta G^{CT(c)}$ kJ mol <sup>-1</sup>	$f_{\Delta}^T$ (A)	$f_{\Delta}^T$ (B)	$f_{\Delta}^T$ (C)
1-methoxynaphthalene	251	1.38	-43	0.33	0.34	0.56
acenaphthene	248	1.41	-37	0.41	0.40	0.61
2-methoxynaphthalene	260	1.52	-38	0.44	0.50	0.80
1-methylnaphthalene	249	1.54	-25	0.60	0.56	0.84
1-ethylnaphthalene	250	-	-	0.56	0.57	0.86
2-methylnaphthalene	254	1.52	-32	0.61	0.57	0.91
2-ethylnaphthalene	-	-	-	0.61	0.59	0.88
naphthalene	255	1.63	-22	0.62	0.62 <sup>(d)</sup>	0.92 <sup>(d)</sup>
2-bromonaphthalene	252	1.90	+7	0.68	0.66	0.94
1-fluoronaphthalene	251	-	-	0.71	0.68	0.94
1-bromonaphthalene	247	1.85	+7	0.77	0.73	1.04
1-chloronaphthalene	248	-	-	0.74	0.75	1.01
1-cyanonaphthalene	241	1.95	+22	0.74	0.75	1.03
benzophenone	287	-	-	0.38 <sup>(e)</sup>	0.33 <sup>(e)</sup>	-
phenazine	186	-	-	0.86 <sup>(e)</sup>	0.82 <sup>(e)</sup>	0.96 <sup>(e)</sup>
acridine	189	-	-	0.82 <sup>(d,e)</sup>	-	-
biphenyl	274	-	-	-	-	0.86 <sup>(e)</sup>

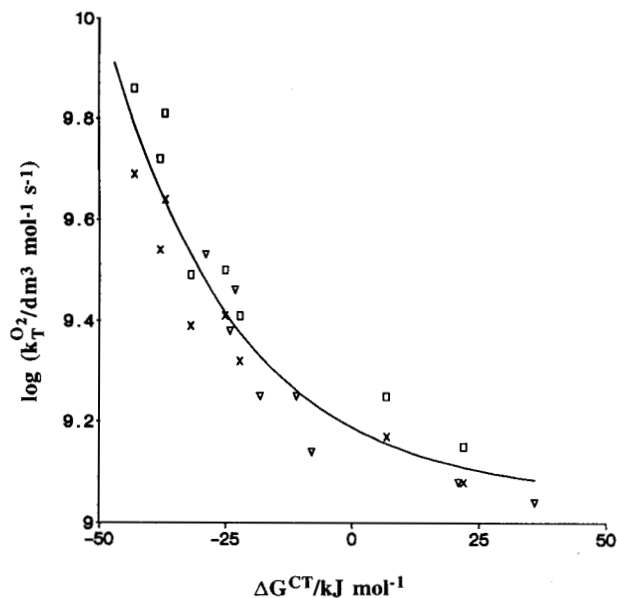
(a) From Refs. 22 and 20; (b) vs. SCE in acetonitrile from Refs. 34 and 20; (c) calculated for acetonitrile and benzene using Eq. 9 see text; (d) standard value; (e) number refers to  $\phi_{\Delta}$ , not  $f_{\Delta}^T$ .

**Table 2.** Rate constants for oxygen quenching of triplet states of naphthalene derivatives ( $k_T^{O_2}$ ) in acetonitrile, benzene and cyclohexane as solvent.

Sensitizer	Acetonitrile $k_T^{O_2}$ (10 <sup>9</sup> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	Benzene $k_T^{O_2}$ (10 <sup>9</sup> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	Cyclohexane $k_T^{O_2}$ (10 <sup>9</sup> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
1-methoxynaphthalene	7.2	5.0	3.4
acenaphthene	6.5	4.4	2.9
2-methoxynaphthalene	5.3	3.5	2.4
1-methylnaphthalene	3.2	2.6	1.8
1-ethylnaphthalene	3.3	2.6	1.8
2-methylnaphthalene	3.1	2.5	1.8
2-ethylnaphthalene	3.3	2.5	1.8
naphthalene	2.6	2.1	1.4
2-bromonaphthalene	1.8	1.5	1.2
1-fluoronaphthalene	2.2	1.9	1.4
1-bromonaphthalene	1.8	1.5	1.2
1-chloronaphthalene	1.9	1.6	1.3
1-cyanonaphthalene	1.4	1.2	1.1

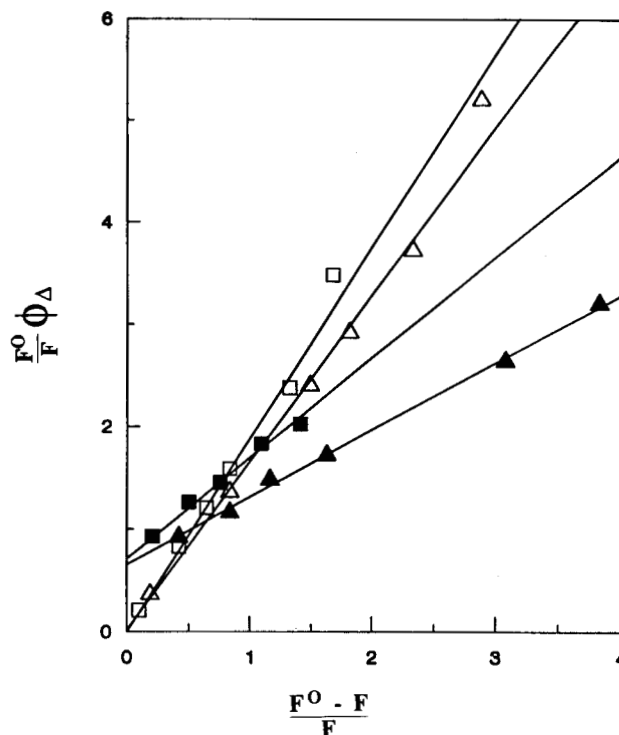
shown that  $\Delta\omega$  equals  $14.5 \pm 1.5$  kJ mol<sup>-1</sup> for 60 exciplexes in hexane and therefore we have used this value of  $\Delta\omega$  in order to estimate values of  $\Delta G^{CT}$  for cyclohexane and taking  $\Delta\omega$  to be close to zero for benzene and acetonitrile<sup>18</sup>.

Figure 1 shows a plot of  $\log k_T^{O_2}$ , versus  $\Delta G^{CT}$  for all three solvents. The limiting slope of this line is indicative of exciplex formation with substantial but not complete charge transfer.

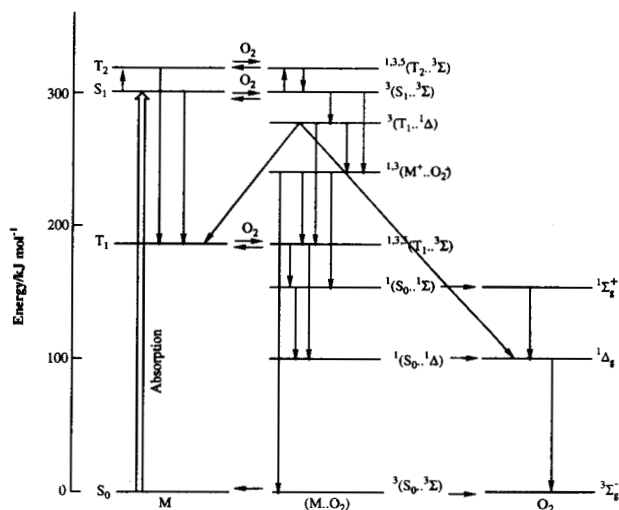


**Figure 1.** Dependence of the rate constants for oxygen quenching of the triplet states on  $\Delta G^{CT}$  for naphthalene derivatives in  $\square$  acetonitrile,  $\times$  benzene and  $\nabla$  cyclohexane.

Typical plots of the data obtained in acetonitrile in accordance with Eq. 7 are shown in Fig. 2. Combining the intercepts with the triplet quantum yields for the various anthracene derivatives allows values of  $f_{\Delta}^T$  to be determined, (see Table 4). The  $f_{\Delta}^T$  values are unity within experimental error for all of the anthracene derivatives studied except for 9-methoxyanthracene in acetonitrile. Thus the efficiency of singlet oxygen production from the triplet states of substituted anthracenes is not affected by changing the solvent polarity except in the case of 9-methoxyanthracene. The difference in behavior between substituted anthracenes and naphthalenes can be ascribed to the fact that the energy of the charge transfer state of the encounter complex between oxygen and the hydrocarbon produced following electron transfer from the hydrocarbon to  $O_2$  is higher than the lowest locally excited triplet state in the case of all the anthracene derivatives except for 9-methoxyanthracene in acetonitrile but is lower in the case of many naphthalene derivatives in all three solvents. Thus the difference in behavior between substituted anthracenes and naphthalenes can be explained in terms of Fig. 3 which shows that the charge transfer states of the complex ( $M..O_2$ ), where M represents aromatic hydrocarbon for a typical anthracene derivative, labeled  $^{1,3}(M^+..O_2^-)$  lie at much higher energies than the lowest locally excited triplet states labeled  $^{1,3,5}(T_1..^3\Sigma)$ . This contrasts with the case of many naphthalene derivatives where the  $^{1,3}(M^+..O_2^-)$  has lower energy than the locally excited triplet state, thus enabling triplet state quenching by oxygen quenching via the complex states  $^{1,3}(T_1..^3\Sigma)$  to  $^{1,3}(M^+..O_2^-)$ , the triplet component of which decays to give  $^3(S_0..^3\Sigma)$  which accounts for  $f_{\Delta}^T$  being less than 1 and  $k_T^{O_2}$  greater than  $k_{diff}/9$



**Figure 2.** Plots to determine  $f_{\Delta}^S$  and  $f_{\Delta}^T$  according to Eq. 7 for 9,10-dicyanoanthracene in cyclohexane,  $\square$ , and in acetonitrile,  $\Delta$ , and for anthracene in cyclohexane,  $\blacktriangle$ , and in acetonitrile,  $\blacksquare$ .



**Figure 3.** Energy level diagram for a typical meso substitute in anthracene M, molecular oxygen  $O_2$  and the contact complex ( $M..O_2$ ).

in several cases<sup>18</sup>. Table 3 shows that  $E_{CT}$  is very close to  $E_{T_1}$  in the case of 9-methoxyanthracene and 9-methylanthracene. The values of  $E_{CT}$  are calculated from literature values of the oxidation potentials and are subject to an uncertainty of at least  $\pm 15 \text{ kJ mol}^{-1}$ . We suggest that the exceptional behavior of 9-methoxyanthracene strongly indicates that in this case the energy of the  $^3(M^+..O_2^-)$  is lower than the locally excited triplet state, while in the case

9-methylanthracene the energy levels are reversed, *i.e.* due to experimental errors the relative energies of  $E_{CT}$  and  $E_{T1}$  are the opposite of that shown in Table 3 in the case of 9-methoxyanthracene and 9-methylanthracene.

Values of  $f_T^{O_2}$  measured using Eq. 5 are given in Table 4 and show that for meso-anthracene derivatives in acetonitrile the efficiency of triplet state production from oxygen quenching of singlet states is either equal to or lower than

in cyclohexane where for the five cases measured  $f_T^{O_2} = 1$ . Previously Potashnik *et al.*<sup>29</sup> have shown that  $f_T^{O_2}$  values for acetonitrile solutions of pyrene and phenanthrene are 0.6 and 0.55 respectively and smaller than values they obtained for these compounds in toluene as solvent. Our value for anthracene in acetonitrile of  $f_T^{O_2} = 0.83 \pm 0.12$  is, within experimental error, equal to that reported by Potashnik *et al.* for this molecule.

**Table 3.** Energies of singlet,  $E_{S_1}$  and triplet,  $E_{T_1}$  and  $E_{T_2}$ , and charge transfer,  $E_{CT}$ , states and rate constants  $k_S^{O_2}$  ( $k_T^{O_2}$ ) for quenching of singlet and triplet states respectively of anthracene derivatives by oxygen in cyclohexane solution.

Compounds	$E_{S_1}^{(a)}$	$E_{T_1}^{(a)}$	$E_{T_2}^{(a)}$	$E_{CT}^{(b)}$	$k_S^{O_2 (c)}$ ( $k_T^{O_2}$ )
					( $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )
kJ mol <sup>-1</sup>					
9-methoxyanthracene	309	173	323	177	27 (3.2)
9-methylanthracene	310	173	322	168	27 (3.3)
9,10-diphenylanthracene	305	171	319	193	17 (---)
9-phenylanthracene	312	176	320	184	19 (3.4)
Anthracene	318	178	323	189	25 (3.4)
9,10-dibromoanthracene	297	168	316	215	24 (2.7)
9,10-dichloroanthracene	298	169	316	-	19 (2.7)
9-cyanoanthracene	299	169	316	227	6.7 (---)
9,10-dicyanoanthracene	286	175	311	258	4.7 (---)

(a) From Ref. 18; (b)  $E_{CT} = F(E_{OX}^M - E_{O_2}^{red})$ ; (c) from Ref. 35.

**Table 4.** The efficiencies of singlet oxygen production from oxygen quenching of singlet and triplet state  $f_{\Delta}^S$  and  $f_{\Delta}^T$  and the fraction of singlet states quenched by oxygen which give triplet states  $f_T^{O_2}$  for anthracene derivatives in acetonitrile and cyclohexane.

Compounds		$f_{\Delta}^T$	$f_{\Delta}^S$	$f_T^{O_2 (a)}$
9-methoxyanthracene	acetonitrile	$0.33 \pm 0.2$	$0.33 \pm 0.2$	$0.87 \pm 0.17^{(b)}$
	cyclohexane	$1.0 \pm 0.1$	$0.3 \pm 0.1$	$1.0^{(c)}$
9-methylanthracene	acetonitrile	$1.0 \pm 0.1$	$0 \pm 0.1$	$0.62 \pm 0.1$
	cyclohexane	1.0	$0.1 \pm 0.1$	$1.0 \pm 0.1$
9,10-diphenylanthracene	acetonitrile	$1.0 \pm 0.2$	$0.1 \pm 0.1$	$0.57 \pm 0.14$
	cyclohexane	$1.0 \pm 0.1$	$0.0 \pm 0.1$	$1.0 \pm 0.1$
9-phenylanthracene	acetonitrile	$\sim 1.0$	$0.1 \pm 0.1$	$0.6 \pm 0.1^{(b)}$
	cyclohexane	$\sim 1.0$	$0.2 \pm 0.1$	$1.0^{(c)}$
Anthracene	acetonitrile	0.9	$0 \pm 0.1$	$0.83 \pm 0.12$
	cyclohexane	1.0	$0 \pm 0.1$	$1.0 \pm 0.1$
9,10-dibromoanthracene	acetonitrile	$0.9 \pm 0.1$	$0.2 \pm 0.2$	$0.90 \pm 0.1^{(b)}$
	cyclohexane	1.0	$0.8 \pm 0.2$	$1.0^{(c)}$
9,10-dichloroanthracene	acetonitrile	1.0	$0.3 \pm 0.1$	$0.70 \pm 0.11$
	cyclohexane	1.0	$0.6 \pm 0.1$	$1.0 \pm 0.1$
9-cyanoanthracene	acetonitrile	$\sim 1$	$0.25 \pm 0.15$	$0.85 \pm 0.15^{(b)}$
	cyclohexane	$\sim 1.0$	$0.5 \pm 0.1$	$1.0^{(c)}$
9,10-dicyanoanthracene	acetonitrile	$1.0 \pm 0.1$	$0.52 \pm 0.1$	$1.0 \pm 0.1^{(b)}$
	cyclohexane	1.0	$1.0 \pm 0.1$	$1.0 \pm 0.1$

(a) Measured using Eq. 8 unless otherwise indicated; (b) calculated values based on the measured solvent dependence of  $k_S^{O_2}$  see Ref. 38; (c) assumed values since all measured values in cyclohexane are  $1.0 \pm 0.1$ .



The efficiency of singlet oxygen production from the first excited singlet state  $f_{\Delta}^S$  varies from close to zero, in the case of anthracene, to unity for 9,10-dicyanoanthracene in cyclohexane. It is interesting to note, see Table 4, that  $f_{\Delta}^S$  values in acetonitrile solvent are lower than in cyclohexane and vary from 0 to 1/2. It follows therefore, that in acetonitrile the oxygen quenching of the excited singlet states occurs through an additional channel, Reaction 6 in Scheme 1, which is negligible in cyclohexane. Previously we have demonstrated<sup>18</sup> that the magnitude of  $f_{\Delta}^S$  in cyclohexane is determined by competition between the two processes which form different triplet encounter complexes, namely  ${}^3(T_2..{}^3\Sigma)$  and  ${}^3(T_1..{}^1\Delta)$ , from the initially formed complex,  ${}^3(S_1..{}^3\Sigma)$  as illustrated in Fig. 3 which shows the various possibilities, with the value of  $f_{\Delta}^S$  depending on the fractional production and dissociation of this latter complex  ${}^3(T_1..{}^1\Delta)$  to form singlet oxygen, a process which yields at the same time the molecular triplet state of the anthracene derivative<sup>18</sup>. The two competing processes are summarized as Reactions 4 and 5 in Scheme 1. Other workers<sup>6</sup> have also demonstrated the importance of the energy of the  $T_2$  state in determining the singlet oxygen production during quenching by oxygen of singlet states. The work presented here establishes the occurrence of Reaction 6 for anthracene derivatives in polar solvents and suggest that a considerable further 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 states of even anthracene derivatives.

## Conclusions

In this paper we have shown that oxygen quenching of excited singlet state is not always diffusion controlled and the rate constants for oxygen quenching of triplet states sometimes exceed the value of 1/9 diffusion controlled. We have clearly demonstrated that oxygen quenching of singlet and triplet states can produce  $O_2({}^1\Delta_g)$  with variable efficiency and oxygen quenching of excited singlet states yield triplet states with less than unit efficiency in polar solvents. The data presented are consistent with the formation of charge transfer states during quenching being an important determining factor.

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