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Singlet oxygen formation efficiencies following quenching of excited singlet and triplet states of aromatic hydrocarbons by molecular oxygen

Ayman A. Abdel-Shafi, David R. Worrall, Francis Wilkinson*

Department of Chemistry, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

Abstract

Rate constants for quenching by molecular oxygen of excited singlet and triplet states, $k_{\mathrm{S}}^{\mathrm{O}_2}$ and $k_{\mathrm{T}}^{\mathrm{O}_2}$, respectively, of 11 aromatic hydrocarbons in cyclohexane are reported. Measured values of $k_{\mathrm{S}}^{\mathrm{O}_2}$ are in the range 0.44 to $2.5 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ and are therefore in many cases close to k_{d}, the diffusion controlled value of $2.8 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. The fraction of excited singlet states quenched by oxygen which result in triplet states, $f_{\mathrm{T}}^{\mathrm{O}_2}$, was measured for all the compounds and found to be unity. The efficiencies of singlet oxygen production during oxygen quenching of the excited singlet and triplet states, f_{Δ}^{S} and f_{Δ}^{T}, respectively, were also measured. Values of f_{Δ}^{S} were shown to be 0, within experimental error, for all compounds except perylene for which $f_{\Delta}^{\mathrm{S}} = 0.28 \pm 0.05$. Values of $k_{\mathrm{T}}^{\mathrm{O}_2}$ vary from 0.46 to $2.32 \times 10^{9}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. Thus, $k_{\mathrm{T}}^{\mathrm{O}_2}/k_{\mathrm{d}}$ was found to be less than one-ninth for all the compounds studied. Three different methods were used to measure f_{Δ}^{T} values, which were found to range from 0.57 to 1. Combination of the total quenching rate constants with the fractional efficiencies allows separate net quenching rate constants to be obtained for the various oxygen quenching pathways. Quenching of both excited singlet and triplet states, with and without energy transfer, are shown to be 'charge-transfer assisted' and mechanisms accounting for these results are discussed.

Keywords: Singlet oxygen; Quenching; Aromatic hydrocarbons; Energy transfer efficiency

1. Introduction

One of the many major contributions made to science by Nobel Laureate Lord George Porter was in the early 1970s when he and his co-workers published two seminar papers on the mechanism of oxygen quenching of the electronically excited states of aromatic hydrocarbons [1,2]. These papers established: (i) the importance of spin statistical factors in the quenching of triplet states by oxygen demonstrating that the rate constants for quenching, $k_{\mathrm{T}}^{\mathrm{O}_2}$, of molecules with low triplet energies are close to one-ninth of the diffusion controlled value; (ii) that quenching of triplet states of compounds with high energies give rate constants which are inversely proportional to triplet energy and (iii) that quenching probabilities increase in polar solvents implying the involvement of charge-transfer interactions. The mechanism given in [2] (see Scheme 1, where k_{d} is the diffusion-controlled rate constant and $k_{-\mathrm{d}}$ the unimolecular rate constant for separation of encounter pairs), sometimes expanded [3–5] (see later) to include excited complexes in which there is substantial charge-transfer interaction, between oxygen and the compound, M and the possibility of intersystem crossing between the channels (1a) (1b), (2) and (3) is still useful today.

After almost 30 years of further research effort, the following comments can be made concerning Scheme 1, whilst acknowledging that there are still aspects of the oxygen quenching of excited states which are not fully understood. Bodesheim et al. [6] have recently developed methods for determining the separate rate constants, $k_{\mathrm{et}}^{1\Sigma}$, $k_{\mathrm{et}}^{1\Delta}$ and $k_{\mathrm{cisc}}^{3\Sigma}$ for oxygen quenching in carbon tetrachloride of triplet states via steps (1a), (1b) and (2) which results in the formation of the $\mathrm{O}_2^*(^1\Sigma_{\mathrm{g}}^+)$, $\mathrm{O}_2^*(^1\Delta_{\mathrm{g}})$ and $\mathrm{O}_2(^3\Sigma_{\mathrm{g}}^-)$ states of oxygen, respectively. They have shown, for 13 sensitisers with triplet energies in the range $140\,\mathrm{kJ\,mol^{-1}} \leq E_{\mathrm{T}} \leq 309\,\mathrm{kJ\,mol^{-1}}$, that these separate rate constants decrease with increasing excess energy, ΔE, in a common way. For all three quenching paths, plots of $\log(k_{\mathrm{m}}/m)$ versus ΔE, where m is the spin multiplicity of the oxygen state produced, can be superimposed for $\Delta E \leq 220\,\mathrm{kJ\,mol^{-1}}$ and the common curve shows a less steep dependence on ΔE than that given by Siebrand's [7–9] energy gap equation for radiationless transitions which was derived to fit data obtained from strongly bound aromatic hydrocarbons rather than for the much weaker bound excited state complexes which undergo the radiationless transitions leading to oxygen quenching as shown in Scheme 1.

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* Corresponding author. Fax: +44-1509-223925.
E-mail address: f.wilkinson@lboro.ac.uk (F. Wilkinson).

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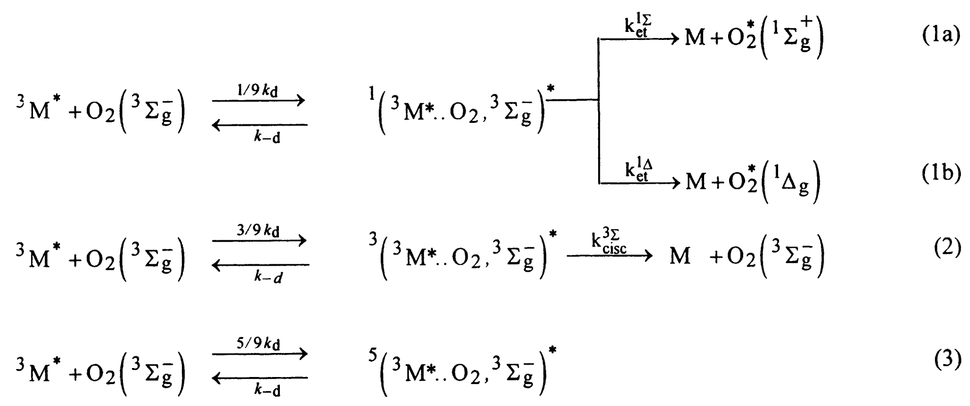


Scheme 1.

Evidence that $k_T^{O_2}$ exceeds $k_d/9$, especially in polar solvents, when the energy of the charge-transfer state of the $M\ldots O_2$ complex lies below the triplet state energy of M, has been reported by several groups [3–5,10–15]. Although there is no direct path for spin allowed decay of the collision complex $^5(^3M^*\ldots O_2,{}^3\Sigma_g^-)^*$, there is evidence that in some cases $k_T^{O_2}$ can be $>4k_d/9$. In particular, Darmanyan et al. [15] have reported extraordinary high rate constants for the quenching of triplet states of strong electron donating amines by oxygen in cyclohexane with values approaching the diffusion controlled limit. The highest reported value is $2.2\times10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ for *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylendiamine (TMPD) in cyclohexane. *Note*: A value for k_d for aromatic hydrocarbons and oxygen in cyclohexane of $2.8\times10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ has been suggested [16] since this is the average value for the rate constants for oxygen quenching of the lowest excited singlet states, $k_S^{O_2}$, for a selection of 16 aromatic hydrocarbons measured in cyclohexane at 25°C. It is interesting to note that Porter and co-workers [1] reported $k_S^{O_2}$ values for eight aromatic hydrocarbons in cyclohexane ranging from 2.5 to $3.1\times10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ which also average to give $2.8\times10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$.

In most solutions, even including CCl_4 where emission from $O_2^*(^1\Sigma_g^+)$ can be detected, $O_2^*(^1\Sigma_g^+)$ has been shown to decay rapidly with unit efficiency [6,17–20] to produce $O_2^*(^1\Delta_g)$. It is well known that $O_2^*(^1\Delta_g)$, which henceforth we shall refer to simply as singlet oxygen, is produced with varying efficiency in solution as a consequence of oxygen quenching of both excited singlet and triplet states. The mechanism given in Scheme 2 shows the minimum number of steps needed to explain oxygen quenching in solution. *Note*: Step 6 includes direct production of $O_2^*(^1\Delta_g)$ from oxygen quenching as well as $O_2^*(^1\Delta_g)$ formed from any $O_2^*(^1\Sigma_g^+)$ resulting initially. Step 7 includes all quenching which is not due to catalysed intersystem crossing, with or without energy transfer, and step 10 includes all quenching of the triplet state which does not lead to singlet oxygen.

The fraction of excited singlet states quenched by oxygen which yields singlet oxygen, f_Δ^S and the fraction of excited singlet states quenched by oxygen which results in triplet states, $f_T^{O_2}$ defined in Scheme 2 are rarely reported. However, in 1971, Potashnik et al. [21] showed that $f_T^{O_2}$ was unity in the case of eight aromatic hydrocarbons in toluene as solvent, but where values were measured in the polar solvent acetonitrile, oxygen quenching of excited singlet states did not always result in the production of triplet states. These authors [21] reported values of $f_T^{O_2}$ as low as 0.55 and 0.6 for pyrene and phenanthrene, respectively, in acetonitrile. More recently, values of $f_T^{O_2}$ less than unity have been reported for several aromatic hydrocarbons in acetonitrile by Sato et al. [22], whilst for anthracene and several of its derivatives, $f_T^{O_2}$ were found to be unity in cyclohexane and to vary from 0.6 to 1 in acetonitrile [23,24]. Values of $f_T^{O_2}$ less than unity are usually explained as arising from quenching due to charge-transfer interactions, which have often been shown not to give rise to free ions even in polar solvents [22,24,25].

In 1990, McLean et al. [26] measured the efficiencies of singlet oxygen production f_Δ^S and f_Δ^T from the excited singlet and triplet states of seven compounds in benzene solution. These authors reported f_Δ^S values of 0 in all cases except for pyrene and perylene, for which values of 0.13 and 0.56, respectively, were reported. However, these authors assumed $f_T^{O_2}$ values of unity, as did Usui et al. [27] who reported f_Δ^S and f_Δ^T values for some aromatic hydrocarbons in cyclohexane. Previously, we have reported the efficiencies of singlet oxygen production from the excited singlet and triplet states of a series of anthracene and eight of its meso-derivatives. Invariably, the values of f_Δ^S measured in acetonitrile [24] as a solvent are lower than those reported in cyclohexane [23] for the same compounds. The relative position of the second excited triplet state T_2 has been shown to be crucial in determining whether energy transfer occurs from excited singlet states even when this is energetically possible [23–25,27].

The fraction of triplet states quenched by oxygen which yield singlet oxygen, f_Δ^T, has been measured for many

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

$$\left.\begin{array}{ll} 2. & {}^1\mathrm{M}^* \xrightarrow{k_\mathrm{f}} {}^1\mathrm{M} + h\nu_\mathrm{f} \\ 3. & {}^1\mathrm{M}^* \xrightarrow{k_\mathrm{ic}} {}^1\mathrm{M} \\ 4. & {}^1\mathrm{M}^* \xrightarrow{k_\mathrm{isc}} {}^3\mathrm{M}^* \end{array}\right\} k_\mathrm{SD} = k_\mathrm{f} + k_\mathrm{ic} + k_\mathrm{isc} \qquad \begin{array}{l} \Phi_\mathrm{F}^0 = k_\mathrm{f}/k_\mathrm{SD} \\ \Phi_\mathrm{T}^0 = k_\mathrm{isc}/k_\mathrm{SD} \end{array}$$

$$\left.\begin{array}{ll} 5. & {}^1\mathrm{M}^* + {}^3\mathrm{O}_2 \xrightarrow{k_{\mathrm{S}\Delta}} {}^3\mathrm{M}^* + {}^1\mathrm{O}_2^* \\ 6. & {}^1\mathrm{M}^* + {}^3\mathrm{O}_2 \xrightarrow{k_\mathrm{ST}} {}^3\mathrm{M}^* + {}^3\mathrm{O}_2 \\ 7. & {}^1\mathrm{M}^* + {}^3\mathrm{O}_2 \xrightarrow{k_\mathrm{SO}} \text{Quenching} \end{array}\right\} k_\mathrm{S}^{\mathrm{O}_2} = k_{\mathrm{S}\Delta} + k_\mathrm{ST} + k_\mathrm{SO} \qquad \begin{array}{l} f_\Delta^\mathrm{S} = k_{\mathrm{S}\Delta} / k_\mathrm{S}^{\mathrm{O}2} \\ f_\mathrm{T}^{\mathrm{O}2} = (k_{\mathrm{S}\Delta} + k_\mathrm{ST}) / k_\mathrm{S}^{\mathrm{O}2} \\ \Phi_\mathrm{F}^0 / \Phi_\mathrm{F} = F^0 / F = 1 + k_\mathrm{S}^{\mathrm{O}2}[\mathrm{O}_2] / k_\mathrm{SD} \end{array}$$

$$\begin{aligned} P_\mathrm{S}^{\mathrm{O}2} &= k_\mathrm{S}^{\mathrm{O}2}[\mathrm{O}_2] / (k_\mathrm{SD} + k_\mathrm{S}^{\mathrm{O}2}[\mathrm{O}_2]) \\ &= (F^0 - F) / F^0 \end{aligned}$$

$$8.\quad {}^3\mathrm{M}^* \xrightarrow{k_\mathrm{TD}} {}^1\mathrm{M}$$

$$\left.\begin{array}{ll} 9. & {}^3\mathrm{M}^* + {}^3\mathrm{O}_2 \xrightarrow{k_{\mathrm{T}\Delta}} {}^1\mathrm{M} + {}^1\mathrm{O}_2^* \\ 10. & {}^3\mathrm{M}^* + {}^3\mathrm{O}_2 \xrightarrow{k_\mathrm{TO}} \text{Quenching} \end{array}\right\} k_\mathrm{T}^{\mathrm{O}_2} = k_{\mathrm{T}\Delta} + k_\mathrm{TO} \qquad \begin{array}{l} f_\Delta^\mathrm{T} = k_{\mathrm{T}\Delta} / k_\mathrm{T}^{\mathrm{O}2} \\ P_\mathrm{T}^{\mathrm{O}2} = k_\mathrm{T}^{\mathrm{O}2}[\mathrm{O}_2] / (k_\mathrm{TD} + k_\mathrm{T}^{\mathrm{O}2}[\mathrm{O}_2]) \end{array}$$

$$\left.\begin{array}{ll} 11. & {}^1\mathrm{O}_2^* \xrightarrow{k_{\Delta\mathrm{d}}} {}^3\mathrm{O}_2 \\ 12. & {}^1\mathrm{O}_2^* \xrightarrow{k_{\Delta\mathrm{p}}} {}^3\mathrm{O}_2 + h\nu_\mathrm{p} \end{array}\right\} k_\Delta = k_{\Delta\mathrm{p}} + k_{\Delta\mathrm{d}}$$

Scheme 2.

molecules [28] and shown to depend on several factors including the excited state energy, the nature of the excited state, the redox potential of the excited state and the nature of the solvent [4,5,11,12,24,25,28–33]. Recently, values of $k_\mathrm{T}^{\mathrm{O}_2}$ and f_Δ^T were reported by us and shown to be inversely correlated for a range of substituted biphenyls [4,5] and naphthalenes [10,33] in acetonitrile, benzene, and cyclohexane. Both $k_\mathrm{T}^{\mathrm{O}_2}$ and f_Δ^T show a pronounced sensitivity to the oxidation potential of the derivative and to the solvent polarity. It was demonstrated that the quenching rate constants increase as the oxidation potential of the derivative decreases and increase as the solvent polarity increases, whereas the efficiencies of singlet oxygen production increase with the oxidation potential and decrease with increasing solvent polarity. Once again in this work, it was demonstrated that free ions were not produced during oxygen quenching. The sensitivity to the oxidation potential is most clearly seen when results from a set of derivatives with almost constant triplet energy, size, etc. are compared. However, Grewer and Brauer [11] have shown a similar dependence is apparent for a wider range of aromatic compounds in toluene as solvent.

Recently, we have reported [25] the efficiencies of singlet oxygen production from the singlet and triplet states for 12 aromatic hydrocarbons in acetonitrile. We have shown that in acetonitrile, the fraction of excited singlet states quenched by oxygen which results in triplet states, $f_\mathrm{T}^{\mathrm{O}_2}$, varies from 0.49 to 1, and f_Δ^S is 0 for eight of the compounds and varies from 0.25 to 0.30 for the other four compounds. In this paper, we report measurements of the efficiencies of formation of singlet oxygen during oxygen quenching of electronically excited singlet and triplet states of these aromatic hydrocarbons in cyclohexane with a view to comparing results with those previously determined in the polar solvent acetonitrile. It is hoped that an explanation can be found for the observed variations of these efficiencies for different aromatic hydrocarbons and for changes observed on changing from polar to non-polar solvents.

2. Experimental

2.1. Materials

Acenaphthene (Aldrich, purity 99%), anthracene (Sigma, purity ≥99%), biphenyl (Aldrich, purity 99%), chrysene (Aldrich, zone refined, purity 98%), 1,2,3,4-dibenzanthracene (DBA, Koch Light, pure), fluoranthene (Aldrich, purity 99%), naphthalene (Aldrich, Scintillation Grade, Gold Label), perylene (Aldrich, purity 99.5%), phenanthrene (Aldrich, purity 99.5%), pyrene (Aldrich, purity 99%), 1-iodopropane (Aldrich, purity 99%), acridine (Aldrich, purity 99%), 2′-acetonaphthone (Aldrich), benzophenone (Aldrich, Gold Label) and cyclohexane (Aldrich, Spectrophotometric Grade) were all used as received. Triphenylene (Aldrich, purity 98%) was recrystallised from toluene. Phenazine (Aldrich) was recrystalised from methanol.

2.2. Apparatus

Ground state absorption spectra were measured using a Hewlett-Packard 8453 single beam photodiode array spectrometer. Steady state luminescence measurements were carried out using a Spex FluoroMax spectrofluorophotometer.

For singlet oxygen luminescence measurements, the third and fourth harmonics of a Lumonics Q-switched Nd:YAG laser (HY 200, 8 ns) were employed for excitation at 355 and 266 nm, respectively. For Φ_Δ measurements, air was removed from the solutions by freeze-pump-thaw cycles and then pure oxygen at different pressures was added to solutions at room temperature and these were allowed to equilibrate. The steady state fluorescence intensity was measured from each solution and time resolved singlet oxygen luminescence (1270 nm) was detected using a Judson Germanium photodiode (G-050, active diameter ~0.5 cm) following laser excitation with energies which did not exceed 0.5 mJ per pulse. Individual singlet oxygen luminescence traces were signal averaged and were fitted using a single exponential function to yield the luminescence intensity I_0 at $t = 0$. The luminescence intensity, I_0 at zero time was plotted against the laser fluence. The slopes obtained from these straight line plots were compared with those obtained from optically matched standards in the same solvent thereby yielding relative Φ_Δ values. Phenazine ($\Phi_\Delta = 0.96$) was used as a standard for excitation at 355 and 266 nm and, in addition, we found it convenient to use naphthalene excited at 266 nm as a secondary standard with ($\Phi_\Delta = 0.80 \pm 0.04$). Using this value, we found good agreement with literature values for Φ_Δ in the case of pyrene [34].

The same laser mentioned above was used as the excitation source for kinetic absorption measurements with a 300 W Xenon arc lamp as the analysing source. Full details of the laser flash photolysis instrument has been given previously [35]. The pseudo-first-order rate constant for triplet state decay, k_{obs}, was measured using different oxygen concentrations. The rate constants $k_{\mathrm{T}}^{\mathrm{O_2}}$ for oxygen quenching of the triplet states were determined using Eq. (1)

$$k_{\mathrm{obs}} = k_{\mathrm{T}\Delta} + k_{\mathrm{T}}^{\mathrm{O_2}}[\mathrm{O_2}] \qquad (1)$$

where k_{obs} and $k_{\mathrm{T}\Delta}$ are the first-order constants for decay of triplet–triplet absorption at the absorption maximum for each compound in the presence and absence of oxygen, respectively.

Slopes of Stern–Volmer plots obtained from fluorescence intensity measurements using air and oxygen saturated solutions were combined with literature fluorescence lifetimes to give the rate constants for oxygen quenching of the singlet states, $k_{\mathrm{S}}^{\mathrm{O_2}}$.

3. Results and discussion

Values of the rate constants for oxygen quenching in cyclohexane of the lowest excited singlet and triplet states, $k_{\mathrm{S}}^{\mathrm{O_2}}$ and $k_{\mathrm{T}}^{\mathrm{O_2}}$, respectively, are given in Table 1 along with the energies of the lowest excited singlet states ($E_{\mathrm{S_1}}$), and of the lowest excited triplet states ($E_{\mathrm{T_1}}$) which cover a wide range from 275 to 418 and 148 to 280 kJ mol^{-1}, respectively. The energy difference between the lowest excited singlet and triplet states is >94 kJ mol^{-1} for seven of the compounds and $\leq$94 kJ mol^{-1} for phenanthrene, triphenylene, fluoranthene and chrysene, where $E_{\mathrm{S_1}} - E_{\mathrm{T_1}}$ values are 86, 69, 74 and 92 kJ mol^{-1}, respectively. Since $\mathrm{O_2^*}(^1\Delta_g)$ lies 94 kJ mol^{-1}

Table 1
Photophysical properties of unsubstituted aromatic hydrocarbons in cyclohexane[a]

Compound	$E_{\mathrm{S_1}}$ (kJ mol^{-1})	$E_{\mathrm{T_1}}$[b] (kJ mol^{-1})	$E_{\mathrm{T_2}}$ (kJ mol^{-1})	$E_{\mathrm{M}}^{\mathrm{OX}}$[c] (V) vs. SCE	τ_{S} (ns)	$k_{\mathrm{S}}^{\mathrm{O_2}}/10^9$ (dm^3 mol^{-1} s^{-1})	$k_{\mathrm{T}}^{\mathrm{O_2}}/10^9$ (dm^3 mol^{-1} s^{-1})
Biphenyl	418	274	<392	1.91	17.2[d]	25.0	0.76
Naphthalene	385	253	371	1.62	96.4[e]	25.0	1.09
Acenaphthene	374	250	358	1.31	46.0[e]	22.0	2.32
Phenanthrene	346	260	323	1.59	57.5[e,g]	20.0	1.58
Triphenylene	349	280	328	1.68	38.0[d]	20.0	0.46
Chrysene	331	239	307	1.45	44.7[f,g]	20.0	1.10
Pyrene	322	203	275	1.22	45.0[e]	25.0	1.86
Anthracene	318	178	312	1.20	4.9[e]	25.0	2.19
1,2,3,4-DBA	319	213	293	1.37	53.5[e]	15.0	1.58
Fluoranthene	295	221	268	1.61	53.0[e]	4.4	1.49
Perylene	275	148	287	0.97	6.4[e,g]	15.0	1.40

[a] Energies of the excited singlet states: $E_{\mathrm{S_1}}$ (±2 kJ mol^{-1}); energies of the triplet states: $E_{\mathrm{T_1}}$ (±2 kJ mol^{-1}) and $E_{\mathrm{T_2}}$ (±10 kJ mol^{-1}); half-wave oxidation potentials: $E_{\mathrm{M}}^{\mathrm{OX}}$ (±0.1 V) and lifetimes of the excited singlet state: τ_{S}. The rate constants for oxygen quenching of excited singlet and triplet states, $k_{\mathrm{S}}^{\mathrm{O_2}}$ and $k_{\mathrm{T}}^{\mathrm{O_2}}$, respectively, have experimental error of ±10%.

[b] From [39].

[c] From [25].

[d] From [34].

[e] From [16].

[f] From [1].

[g] From [40].

above the ground state it is unlikely that these four sensitisers will produce $O_2^*(^1\Delta_g)$ directly during oxygen quenching of their excited singlet states. However, it is energetically possible to produce $O_2^*(^1\Delta_g)$ by oxygen quenching of both excited singlet and triplet states in the case of the other sensitisers which have $E_{S_1} - E_{T_1}$ and $E_{T_1} > 94\,\mathrm{kJ\,mol^{-1}}$.

According to Scheme 2 values of $f_T^{O_2}$, the fraction of excited singlet states quenched by O2 which gives triplet states can be obtained from the measured ratios of the fluorescence intensities F and F^0 and of the triplet absorbances at time $t = 0$, $A_T^{O_2}$ and $A_T^{O_2}$ of optically matched solutions of each hydrocarbon in the presence and absence of oxygen, respectively, using the following equation [21,28]:

$$\left(\frac{A_T^{O_2}}{A_T^0} - \frac{F}{F^0}\right) = \frac{f_T^{O_2}}{\Phi_T^0}\left(1 - \frac{F}{F^0}\right) \tag{2}$$

Plots according to Eq. (2) are shown in Fig. 1. In the case of perylene, the triplet absorbance in the absence of oxygen A_T^0 is difficult to measure with high accuracy due to the very low triplet yield, Φ_T^0. Therefore, for perylene, its triplet absorbance A_T was measured in the presence of iodopropane, which quenches perylene fluorescence by catalysed intersystem crossing with unit efficiency, and this value was compared to the triplet absorbance observed at the same quenching ratios, F/F^0, for quenching of perylene fluorescence by oxygen. Eq. (3) [25], where the subscripts IP and O2 relate to measurements made in the presence of iodopropane and oxygen, respectively, was used at two different values of F/F^0 to calculate $f_T^{O_2}$.

$$\left(\frac{\Phi_T^0 + (F^0/F) - 1}{A_T(F^0/F)}\right)_{IP} = \left(\frac{\Phi_T^0 + f_T^{O_2}[(F^0/F) - 1]}{A_T(F^0/F)}\right)_{O_2} \tag{3}$$

The $f_T^{O_2}$ values for all the compounds studied are unity within experimental error (see Table 2).

Applying the steady state approximation to the excited states in the mechanism given in Scheme 2 gives Eq. (4) for the quantum yield of singlet oxygen production Φ_Δ, provided $P_T^{O_2} = 1$ for each oxygen concentration used [28].

$$\Phi_\Delta\left(\frac{F^0}{F}\right) = (f_\Delta^S + f_T^{O_2} f_\Delta^T)\left(\frac{F^0}{F} - 1\right) + \Phi_T^0 f_\Delta^T \tag{4}$$

Plots of $\Phi_\Delta(F^0/F)$ versus $[(F^0/F) - 1]$ give good straight lines as shown in Fig. 2. The values obtained for the intercepts $(f_\Delta^T \Phi_T^0)$ and slopes $(f_\Delta^T f_T^{O_2} + f_\Delta^S)$ are collected in Table 2. The error in the intercepts is about 10% and errors in the slopes are <10% in all cases. Combination of the intercepts of the plots shown in Fig. 2 together with the values of the triplet quantum yields as given in Table 2 allows values of f_Δ^T to be determined. Values of f_Δ^T were also obtained using the technique of triplet state population with 100% efficiency by energy transfer from a ketone of higher triplet energy (for details, see [5]). Benzophenone was used as triplet donor in the case of phenanthrene and triphenylene, whilst triplet 2′-acetonaphthone was used to sensitise the production of the triplet states of chrysene, pyrene, 1,2,3,4-DBA, and perylene, prior to oxygen quenching. In the case of fluoranthene and anthracene, which strongly absorb at 355 nm, it was difficult to populate their triplet states exclusively via triplet–triplet energy transfer from a ketone. For these two compounds, their triplet states were populated by enhancing intersystem crossing using $0.5\,\mathrm{mol\,dm^{-3}}$ iodopropane to completely quench all fluorescence, enabling their triplet

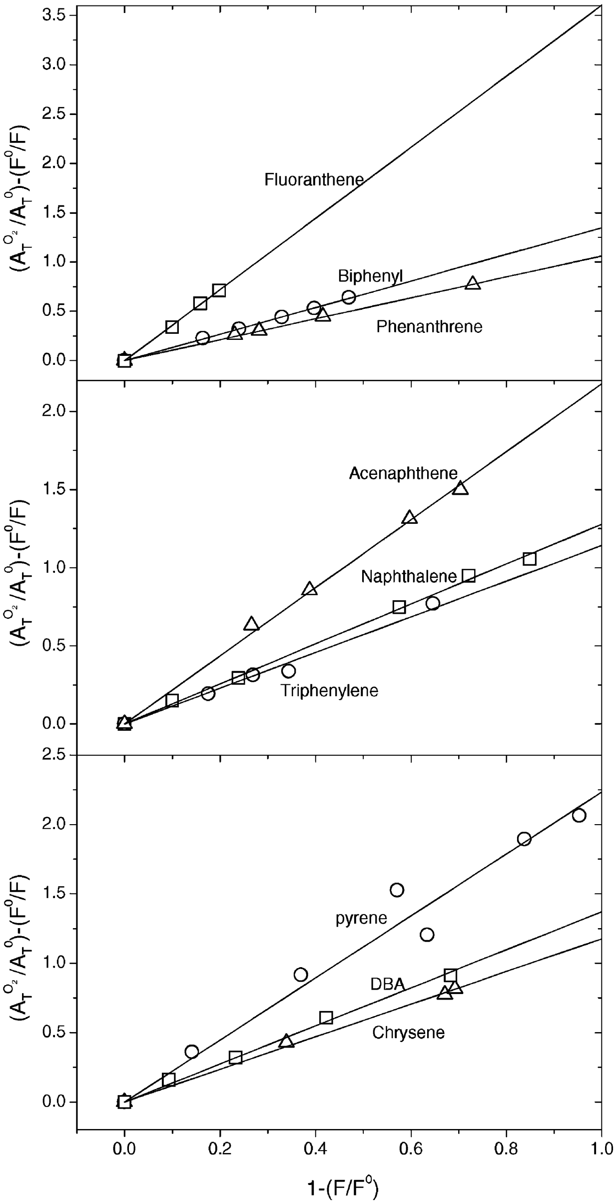


Fig. 1. Plots according to Eq. (2) (see text) for determining, $f_T^{O_2}$, the fraction of the excited singlet states S1 quenched by oxygen which gives triplet states.

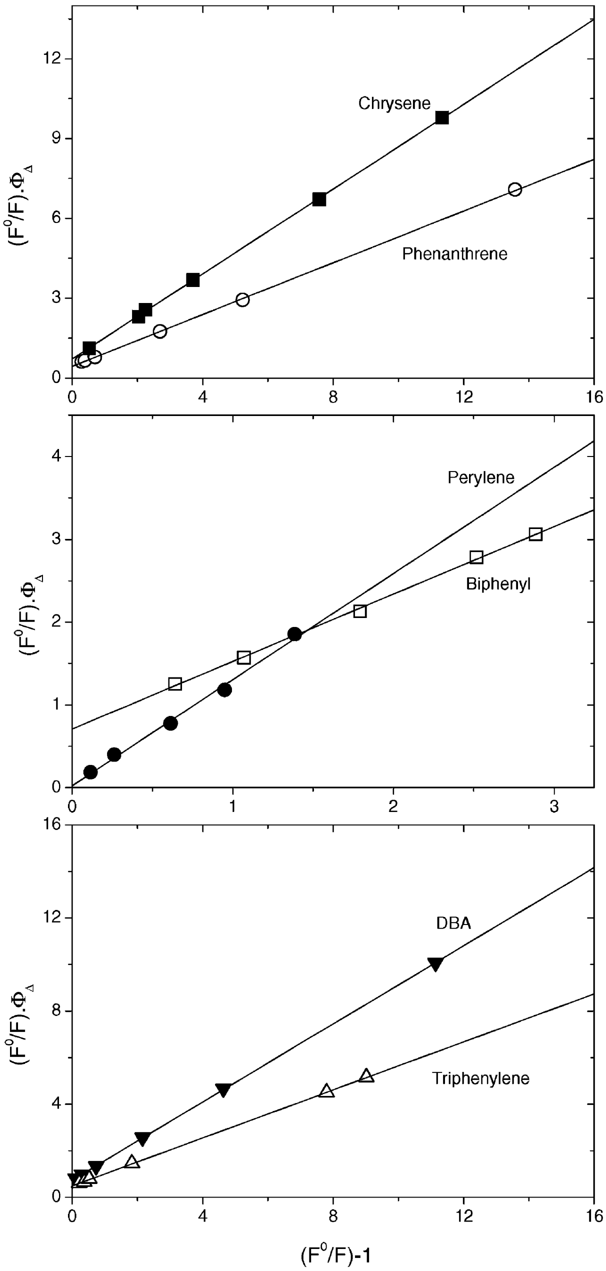


Fig. 2. Plots according to Eq. (5) (see text) for determining the efficiency of singlet oxygen production from the excited singlet (f_Δ^{S}) and triplet states (f_Δ^{T}) of aromatic hydrocarbons in cyclohexane.

states to be produced with an efficiency ≥0.99, prior to oxygen quenching. Measurement of Φ_Δ from these solutions enabled f_Δ^{T} values to be obtained. The values of f_Δ^{T} obtained from the intercept of plots of the type shown in Fig. 2 and by these other two techniques, which do not depend on literature values of Φ_T^{0}, agree within experimental error (see Table 2).

Combination of the measured values of $f_T^{O_2}$ and f_Δ^{T} for each compound allows the determination of f_Δ^{S} using the appropriate value obtained from the slope. The efficiency of singlet oxygen production from the excited singlet states, f_Δ^{S}, was found to be 0, within experimental error, for all sensitisers except perylene. Thus, in the case of all the compounds, the rate constants, $k_{SO} \leq 10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ and $k_{ST} = k_S^{O_2}$ except for perylene for which $k_{ST} = k_S^{O_2}(f_T^{O_2} - f_\Delta^{S}) = 1.1 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ and $k_{S\Delta} = k_S^{O_2} f_\Delta^{S} = 4.2 \times 10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. These results for cyclohexane as solvent contrast with the values obtained for these same hydrocarbons in acetonitrile where k_{ST} values ranging from 0.2 to $3.6 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, k_{SO} values of 0 to $1.6 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ and $k_{S\Delta}$ values in the range 0 to $1 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ were obtained [25]. The fact that these values show a strong solvent dependence supports the suggestion that charge-transfer interactions are involved in oxygen quenching of singlet states of aromatic hydrocarbons [2–5].

3.1. Triplet state quenching

The values of $k_T^{O_2}$ obtained here for unsubstituted aromatic hydrocarbons vary from 0.4 to $2.65 \times 10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ and show a similar dependence on the energy of the first excited triplet state E_{T_1} as those reported previously by Porter and co-workers [2] (see Fig. 3) which also shows the values obtained by us previously for anthracene, biphenyl and naphthalene derivatives in cyclohexane [5,10,24]. It can be seen that the largest values of $k_T^{O_2}$ are close to $k_d/9$ or possibly slightly higher, whereas in the polar solvent acetonitrile, $k_T^{O_2}$ values clearly $>k_d/9$ have been obtained [4,5]. None of these hydrocarbons, or their derivatives, gives $k_T^{O_2}$ that are $>4k_d/9$ even in acetonitrile (see later). This observation and the fact that for anthracene, biphenyl and naphthalene derivatives, where there is little change in the triplet energy E_{T_1}, the largest values of $k_T^{O_2}$ in cyclohexane are for compounds with electron donating substituents, which have relatively low oxidation potentials, once again demonstrates the importance of charge-transfer interactions in determining the quenching efficiencies.

The measured fractional efficiencies f_Δ^{T} can be combined with $k_T^{O_2}$ values to obtain values for $k_{T\Delta}$ and k_{TO}, the net rate constants for oxygen quenching of the excited triplet states with and without energy transfer to produce singlet oxygen, i.e. for steps 9 and 10 in Scheme 2, namely

$$k_{T\Delta} = k_T^{O_2} f_\Delta^{T} \qquad (5)$$

$$k_{TO} = k_T^{O_2}(1 - f_\Delta^{T}) \qquad (6)$$

Values of $k_{T\Delta}$ and k_{TO} evaluated using Eqs. (5) and (6) are given in Table 3. In all but three cases, the values of k_{TO} are subject to large uncertainties since $1 - f_\Delta^{T} = 0.1 \pm 0.1$, for eight of the compounds. In acetonitrile [25], $\log k_{TO}$ values show a linear dependence on ΔG_T^{CT}, the driving force for charge-transfer, a good estimate for which can be calculated from the energy of charge-transfer states corresponding to

Table 2
Experimental values of the slopes ($f_\Delta^T f_T^{O_2} + f_\Delta^S$) and intercepts ($f_\Delta^T \Phi_T^0$) obtained from plots according to Eq. (4)[a]

Compound	Intercept ($f_\Delta^T \Phi_T^0$)	Slope ($f_\Delta^T f_T^{O_2} + f_\Delta^S$)	Φ_T^0	$f_T^{O_2}$	f_Δ^T [b]	f_Δ^T [c]	f_Δ^S
Biphenyl	0.71 ± 0.03	0.81 ± 0.02	0.81[d]	1.00 ± 0.1	0.88	0.75	0.00
Naphthalene	0.64 ± 0.03	0.83 ± 0.01	0.75[e]	0.96 ± 0.1	0.85	0.83	0.01
Acenaphthene	0.27 ± 0.02	0.53 ± 0.01	0.46[d]	1.00 ± 0.1	0.59	0.58	0.00
Phenanthrene	0.44 ± 0.02	0.49 ± 0.01	0.82[d]	0.87 ± 0.1	0.54	0.62	0.02
Triphenylene	0.49 ± 0.01	0.52 ± 0.01	0.86[d]	0.98 ± 0.1	0.57	0.64	0.00
Chrysene	0.72 ± 0.03	0.80 ± 0.01	0.85[e]	1.00 ± 0.1	0.85	0.93	0.00
Pyrene	0.43 ± 0.03	0.80 ± 0.01	0.50[e]	1.10 ± 0.1	0.86	0.99	0.00
Anthracene	0.76 ± 0.03	0.91 ± 0.01	0.71[e]	1.10 ± 0.1	1.0	0.88	0.00
1,2,3,4-DBA	0.73 ± 0.01	0.84 ± 0.01	0.85[f]	1.00 ± 0.1	0.86	0.96	0.00
Fluoranthene	0.37 ± 0.02	0.83 ± 0.01	0.35[g]	1.10 ± 0.1	1.0	0.89	0.00
Perylene	0.02 ± 0.04	1.28 ± 0.05	0.014[h]	1.06 ± 0.1	1.0	0.89	0.28

[a] Triplet quantum yields, Φ_T^0; $f_T^{O_2}$ is the fraction of excited singlet states quenched by oxygen which gives triplet states and f_Δ^S and f_Δ^T are the efficiencies of singlet oxygen production during oxygen quenching of the excited singlet and triplet states, respectively.

[b] f_Δ^T determined from the values of the intercept and triplet quantum yield, error ±10%.

[c] f_Δ^T determined by triplet energy transfer method from a higher ketone or by enhancement of intersystem crossing from the singlet to triplet state by using iodopropane (see text).

[d] From [41].

[e] From [42].

[f] From [39].

[g] In *n*-heptane and in toluene, from [43,44], respectively.

[h] From [45].

the radical ion pair ($M^{+}\ldots O_2{}^{-}$) which is given in [36] by Eq. (7)

$$E_{CT} = F(E_M^{OX} - E_{O_2}^{red}) + C \quad (7)$$

where F is the Faraday constant, E_M^{OX} and $E_{O_2}^{red}$ are the half-wave oxidation potential of the sensitiser and the half-wave reduction potential of $O_2(^3\Sigma_g^-)$, respectively, with both potentials referred to the same standard state. The constant C in Eq. (7), which is often taken as 0 in acetonitrile, depends on the electrostatic interaction energy, which is inversely proportional to the static relative permitivity, ε_r, of the solvent and on the differences in solvation energies of the separate ions and the ion pair. The values of ΔG_S^{CT} and ΔG_T^{CT}, the driving forces for charge-transfer from excited singlet and triplet states, which equal $E_{CT} - E_{S_1}$ and $E_{CT} - E_{T_1}$, respectively, given in Table 3 were calculated taking $C = 0$. The values of k_{TO} in cyclohexane fall on the same curve as they do in case of acetonitrile if the ΔG_T^{CT} values are adjusted by adding $\gamma = 25\,\text{kJ mol}^{-1}$ in the case of the cyclohexane data (see Fig. 4). This adjustment factor, γ, is close to that of $20\,\text{kJ mol}^{-1}$ used previously by us when comparing k_{TO} values for biphenyl derivatives in acetonitrile and cyclohexane, respectively [5]. The plot of $\log k_{TO}$ versus ΔG_T^{CT} shown in Fig. 4 has a slope of $-0.0175\,\text{mol J}^{-1}$ which can be compared with the value of $(-0.434/RT) = -0.178\,\text{mol J}^{-1}$ expected for a reaction involving full electron transfer. A simple interpretation of this smaller slope is that the transition states for oxygen quenching of these triplet states without energy transfer have only

Table 3
Values of the rate constants in cyclohexane for oxygen quenching of the excited triplet states due to energy transfer $k_{T\Delta}$, derived from Eq. (5), and without energy transfer k_{TO}, derived from Eq. (6)[a]

Compound	$k_{T\Delta}$ ($/10^9\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$)	k_{TO} ($/10^9\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$)	ΔG_T^{CT} (kJ mol^{-1})	ΔG_S^{CT} (kJ mol^{-1})
Biphenyl	0.60	0.08	−15.0 ± 2	−158 ± 10
Naphthalene	0.83	0.15	−21.0 ± 2	−153 ± 5
Acenaphthene	1.20	0.86	−48.0 ± 5	−172 ± 10
Phenanthrene	0.87	0.53	−31.0 ± 3	−117 ± 5
Triphenylene	0.23	0.17	−43.0 ± 4	−112 ± 5
Chrysene	0.83	0.15	−24.0 ± 2	−116 ± 5
Pyrene	1.53	0.12	−10.0 ± 1	−129 ± 5
Anthracene	1.94	0	13.0 ± 1	−127 ± 5
1,2,3,4-DBA	1.27	0.13	−6.0 ± 1	−112 ± 5
Fluoranthene	1.32	0	10.0 ± 1	−64 ± 7
Perylene	1.24	0	21.0 ± 2	−106 ± 5

[a] ΔG_T^{CT} and ΔG_S^{CT} are the free energy changes for electron transfer to molecular oxygen from the excited triplet and singlet states, respectively, calculated by Eq. (7) with $C = 0$.

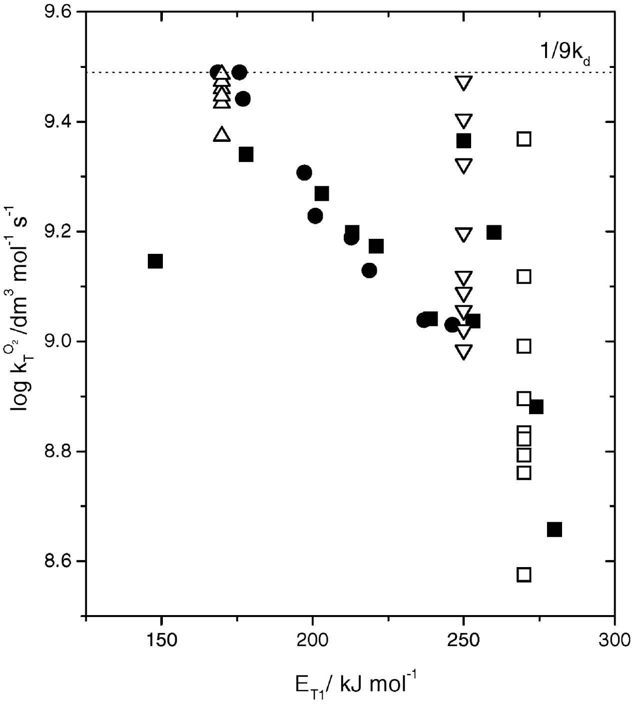


Fig. 3. Dependence of $k_T^{O_2}$, the rate constants for oxygen quenching of the first excited triplet states of the aromatic hydrocarbons in cyclohexane on triplet energy: values obtained in this work (■), Porter's values (●) [1], and those obtained for a series of substituted naphthalenes (□) [10], biphenyls (▽) [5] and anthracenes (△) [23].

~10% charge-transfer character. A similar treatment of the values we obtained previously for k_{TO} in acetonitrile [4,25] gave a value of 13.5% charge-transfer character, whilst Darmanyan et al. [15] have reported a value of 8% charge-transfer character for oxygen quenching of the triplet states of a series of strongly electron donating amines in cyclohexane and benzene. The dependence of the fraction of quenching without energy transfer, $1 - f_\Delta^T$, on ΔG_T^{CT} clearly shows the importance of charge-transfer interactions in determining quenching without energy transfer (see inset in Fig. 4). Thus, the quenching of triplet states by molecular oxygen can be described by Scheme 3 [4,5] based on that originally proposed by Porter and co-workers, i.e. Scheme 1, modified by us to include charge-transfer complexes of oxygen and intersystem crossing between the various quenching channels and competitive non-charge-transfer assisted energy transfer (i.e. also including the step labelled $^1k_\Delta$).

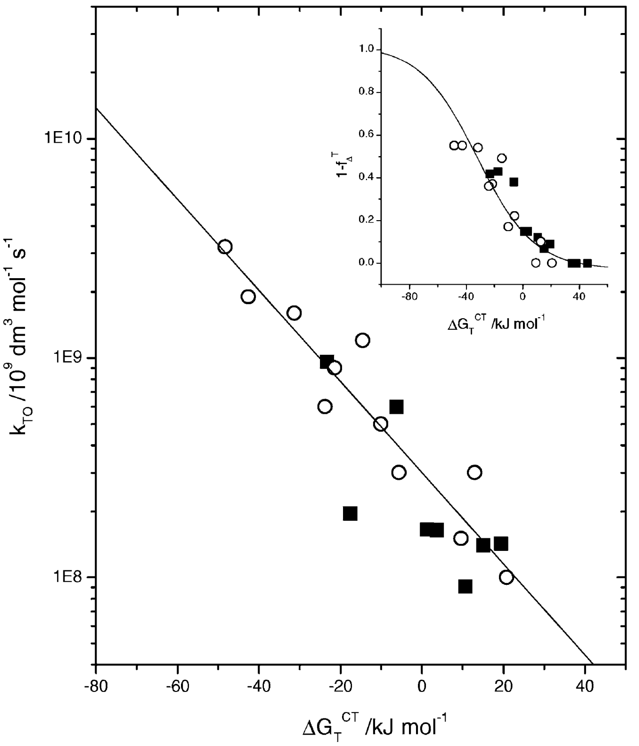
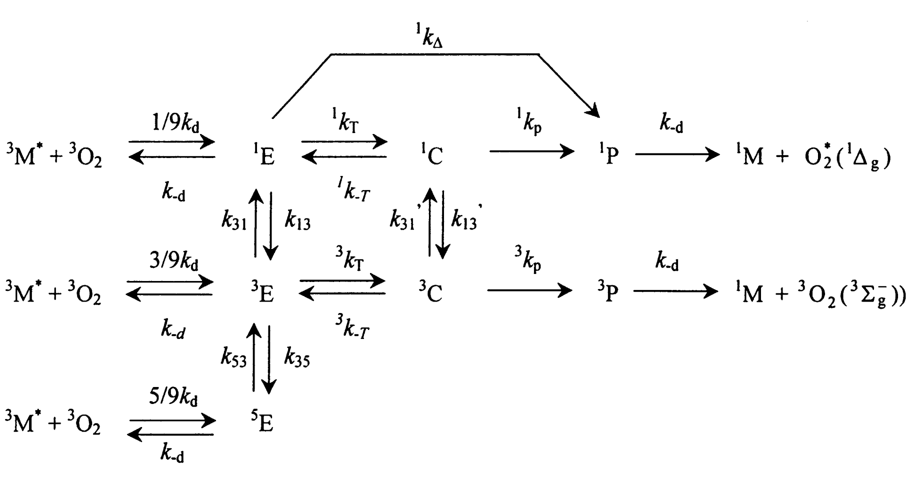


Fig. 4. Dependence of the rate constants for oxygen quenching of the triplet states without energy transfer, k_{TO}, on the free energy change ΔG_T^{CT}. Inset shows the dependence of the fraction of quenching by oxygen without energy transfer $(1 - f_\Delta^T)$ on the free energy change ΔG_T^{CT}. Data in acetonitrile (○) [25] and cyclohexane (■). (*Note*: The values of ΔG_T^{CT} for cyclohexane have been increased by a factor $\gamma = 25\,\mathrm{kJ\,mol^{-1}}$ (see text) in order to superimpose the data).



Scheme 3.

Note: $^1\mathrm{P} = {}^1({}^1\mathrm{M}\ldots\mathrm{O}_2^*({}^1\Delta_\mathrm{g}\,\text{and/or}\,{}^1\Sigma_\mathrm{g}^+))$; $^3\mathrm{P} = {}^3({}^1\mathrm{M}\ldots{}^3\mathrm{O}_2({}^3\Sigma_\mathrm{g}^-))$ and the charge-transfer complexes $^{1,3}\mathrm{C} = {}^{1,3}(\mathrm{M}^+\ldots\mathrm{O}_2{}^-)$ may lie at higher or lower energies than the encounter complexes $^{1,3}\mathrm{E} = {}^{1,3}({}^3\mathrm{M}^*\ldots\mathrm{O}_2, {}^3\Sigma_\mathrm{g}^-)^*$.

It is apparent that for the compounds studied here (see Table 3), $k_{\mathrm{T}\Delta}$ does not exceed $k_\mathrm{d}/9$ and does not show a simple dependence on $\Delta G_\mathrm{T}^\mathrm{CT}$. No clear correlation was found [25] for values of $k_{\mathrm{T}\Delta}$ with $\Delta G_\mathrm{T}^\mathrm{CT}$ for these aromatic compounds in acetonitrile as solvent in contrast to the case for anthracene, biphenyl and naphthalene derivatives, where there is little change in the triplet energy E_{T_1}, and where a correlation between $k_{\mathrm{T}\Delta}$ and $\Delta G_\mathrm{T}^\mathrm{CT}$ was evident [4,5,10]. As indicated in Scheme 3, the net quenching rate constant $k_{\mathrm{T}\Delta}$ would be expected to have a dependence both on $\Delta G_\mathrm{T}^\mathrm{CT}$ and on the excess energy which has to be dissipated during quenching. Schmidt et al. [17] have recently shown that in carbon tetrachloride oxygen quenching of the triplet states of a series of nine naphthalene derivatives of very different oxidation potential but almost constant E_{T_1} clearly show net oxygen quenching rate constants for all three oxygen product states $\mathrm{O}_2^*({}^1\Sigma_\mathrm{g}^+)$, $\mathrm{O}_2^*({}^1\Delta_\mathrm{g})$ and $\mathrm{O}_2({}^3\Sigma_\mathrm{g}^-)$ which depend on charge-transfer interactions and on the excess energy which has to be dissipated during quenching. It is interesting to note that for the series of compounds studied here, that both $\mathrm{O}_2^*({}^1\Sigma_\mathrm{g}^+)$ and $\mathrm{O}_2^*({}^1\Delta_\mathrm{g})$, which have energies of 157 and 94 kJ mol^{-1}, respectively are likely to be produced as a result of quenching by energy transfer, except in the case of perylene where only $\mathrm{O}_2^*({}^1\Delta_\mathrm{g})$ production is energetically possible. In Fig. 5, $\log k_{\mathrm{T}\Delta}$ is plotted against $\Delta E = E_\mathrm{T} - 157\,\mathrm{kJ\,mol^{-1}}$ (*Note*: $\Delta E = E_\mathrm{T} - 94\,\mathrm{kJ\,mol^{-1}}$ was used in the case of perylene) and compared with values obtained by other workers in cyclohexane. Assuming that at a particular excess energy there is a lower limit for $k_{\mathrm{T}\Delta}$ which is likely to have an energy gap dependence as given by Siebrand and co-worker [7–9], a curve has been drawn to fit through the points which give the lowest values for $k_{\mathrm{T}\Delta}$ which can be interpreted as defining values equal to or at least close to the values of $k_{\mathrm{T}\Delta}$ which pertain when charge-transfer assisted energy transfer is zero.

Since the upper experimental limit for $k_{\mathrm{T}\Delta}$ as shown by Fig. 5 is $k_\mathrm{d}/9$, it is apparent that intersystem crossing between the quenching channels in Scheme 3 can be neglected in cyclohexane at room temperature, in which case steady state treatment of all the reactive intermediates in Scheme 3 gives [4,5]

$$k_{\mathrm{T}\Delta} = \frac{k_\mathrm{d}({}^1k_\mathrm{T}{}^1f_\mathrm{p} + {}^1k_\Delta)}{9(k_{-\mathrm{d}} + {}^1k_\mathrm{T}{}^1f_\mathrm{p} + {}^1k_\Delta)} \tag{8}$$

where ${}^1f_\mathrm{p} = {}^1k_\mathrm{p}/({}^1k_{-\mathrm{T}} + {}^1k_\mathrm{p})$ is the fraction of the charge-transfer complex which dissociates to give singlet oxygen. Thus, when ${}^1f_\mathrm{p} = 0$, i.e. when there is no charge-transfer assisted quenching, $k_{\mathrm{T}\Delta} = k_{\mathrm{T}\Delta}^{\Delta E}$ which is given by

$$k_{\mathrm{T}\Delta}^{\Delta E} = \frac{k_\mathrm{d}{}^1k_\Delta}{9(k_{-\mathrm{d}} + {}^1k_\Delta)} \tag{9}$$

Since energy transfer proceeds to produce $\mathrm{O}_2^*({}^1\Sigma_\mathrm{g}^+)$ and/or $\mathrm{O}_2^*({}^1\Delta_\mathrm{g})$, it follows that ${}^1k_\Delta$ will be composed of two contributions each of which is likely to show an energy gap dependence, i.e.

$${}^1k_\Delta = {}^1k_\mathrm{et}^{1\Sigma} + {}^1k_\mathrm{et}^{1\Delta} = PCF(E_\Sigma) + PCF(E_\Delta) \tag{10}$$

where P is the density of states factor and C the electronic factor, and $F(E_\Sigma)$ and $F(E_\Delta)$ are the Franck Condon factors which are dependent on the energy gaps ΔE equal to $(E_{\mathrm{T}_1} - E_{1\Sigma})$ and $(E_{\mathrm{T}_1} - E_{1\Delta})$. The solid curve drawn in Fig. 5 for $k_{\mathrm{T}\Delta}^{\Delta E}$, the rate constant in the absence of charge-transfer assisted quenching, was calculated using Eq. (9) with $k_{-\mathrm{d}} = 5.6 \times 10^{10}\,\mathrm{s^{-1}}$, $PC = 2.5 \times 10^{11}\,\mathrm{s^{-1}}$ and with $F(E_\Sigma)$ and $F(E_\Delta)$ equal to $10^{-0.014(E_{\mathrm{T}_1} - E_{1\Sigma})}$ and $10^{-0.014(E_{\mathrm{T}_1} - E_{1\Delta})}$, respectively. The fitting parameters needed for the product PC, assumed to be constant, and for $F(E)$, to give the solid curve shown in Fig. 5 can be compared with those for allowed radiationless transitions in aromatic hydrocarbons as given and discussed by Birks [37]. It is interesting to note that the value of the Franck Condon factor $F(E)$ for the radiationless transitions within the complexes leading to energy transfer to oxygen of $10^{(-0.014\,\Delta E)}$ gives a less steep dependence on excess energy than that derived by Siebrand for $\mathrm{T}_1 \rightarrow \mathrm{S}_0$ radiationless transitions in aromatic hydrocarbons.

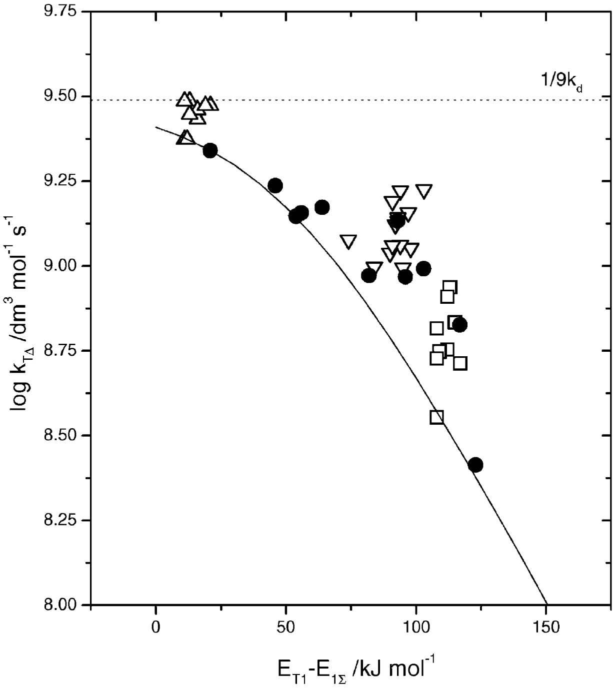


Fig. 5. Dependence of, $k_{\mathrm{T}\Delta}$, the rate constant in cyclohexane for oxygen quenching with energy transfer, of the triplet states of aromatic hydrocarbons (●), naphthalenes (□) [10], biphenyls (▽) [5] and anthracenes (△) [23], on the energy gap $(E_{\mathrm{T}_1} - E_{1\Sigma})$. (*Note*: For perylene, the energy difference is $E_{\mathrm{T}_1} - E_{1\Delta}$ was used, see text).

3.2. Singlet state quenching

In our previous study of oxygen quenching of the fluorescence of anthracene derivatives in cyclohexane [23] and in acetonitrile [24], the crucial importance was demonstrated of internal conversion from the encounter complex $^3(\mathrm{S}_1 \ldots {}^3\Sigma_g^-)$ and the efficiency of formation of the triplet encounter complex $^3(\mathrm{T}_2 \ldots {}^3\Sigma_g^-)$ which can undergo internal conversion directly to give $^3(\mathrm{T}_1 \ldots {}^3\Sigma_g^-)$, which can then dissociate to give $^3\mathrm{M}^*(\mathrm{T}_1) + \mathrm{O}_2(^3\Sigma_g^-)$ without energy transfer by-passing the $^3(\mathrm{T}_1 \ldots {}^1\Delta_g)$ state. In this work, phenanthrene, triphenylene, fluoranthene and chrysene would be expected to have $f_\Delta^\mathrm{S} = 0$ since, $E_{\mathrm{S}_1} - E_{\mathrm{T}_1}$ values are $<94\,\mathrm{kJ\,mol^{-1}}$ and this is confirmed by the experiments. The fact that the energy of the $(\mathrm{T}_2 \ldots {}^3\Sigma_g^-)$ state lies above that of $(\mathrm{S}_1 \ldots {}^3\Sigma_g^-)$, in the case of perylene, easily explains why energy transfer becomes likely and f_Δ^S does not equal to 0 in this case. The zero values of f_Δ^S for the other compounds can be attributed to the fact that the second triplet state lies below the first excited singlet state. In the case of pyrene, f_Δ^S has been measured previously in acetonitrile [25], in cyclohexane [27], and in benzene [26] with reported values of 0.30, 0.15 and 0.13, respectively. The values reported here for f_Δ^S for pyrene and fluoranthene in cyclohexane of 0 compared with 0.30 in acetonitrile imply that the production of singlet oxygen during quenching of excited singlet states is also charge-transfer assisted since it is apparent that f_Δ^S increases significantly with solvent polarity.

Previously, we have reported $f_\mathrm{T}^{\mathrm{O}_2}$ values in the range 0.49–1.0 for these aromatic hydrocarbons in acetonitrile [25]. In this work, in cyclohexane, all values of $f_\mathrm{T}^{\mathrm{O}_2}$ are unity within the experimental error. Once again $f_\mathrm{T}^{\mathrm{O}_2}$ values have been shown to be solvent dependent. The contribution to $k_\mathrm{S}^{\mathrm{O}_2}$ of quenching of singlet states without the production of triplet states is obviously negligible when cyclohexane is used as a solvent and yet values of k_SO are considerable in the polar solvent acetonitrile. Sato et al. [22] have commented on the fact that they found for acetonitrile as solvent $f_\mathrm{T}^{\mathrm{O}_2}$ values only decreased when $\Delta G_\mathrm{S}^\mathrm{CT}$ was very exoergic, i.e. less than $-100 \pm 20\,\mathrm{kJ\,mol^{-1}}$ and that $f_\mathrm{T}^{\mathrm{O}_2}$ values then tended to a constant value of about 0.4. The present results demonstrate that if anything $\Delta G_\mathrm{S}^\mathrm{CT}$ has to be even more negative in order for k_SO not to be negligible in cyclohexane. The low value of $4.4 \times 10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ for $k_\mathrm{S}^{\mathrm{O}_2}$ in the case of fluoranthene found here agrees with the literature value [16]. It is worth noting that $\Delta G_\mathrm{S}^\mathrm{CT}$ is the least exoergic in this case, supporting the suggestion by Kikuchi et al. [38] that $k_\mathrm{S}^{\mathrm{O}_2}$ values only become diffusion controlled if charge-transfer assisted quenching can occur. Reported values for $k_\mathrm{S}^{\mathrm{O}_2}$ in cyclohexane are numerous. In their review, Saltiel and Atwater [16] have reported about 50 values for $k_\mathrm{S}^{\mathrm{O}_2}$ in cyclohexane for the quenching of the excited singlet states of aromatic hydrocarbons in cyclohexane with an average of $2.7 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [16]. Although values of $k_\mathrm{S}^{\mathrm{O}_2}$ considerably less than diffusion controlled are rare they do exist, e.g. $k_\mathrm{S}^{\mathrm{O}_2}$ values of 3.6, and $6.9 \times 10^9\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ have been reported by us for 9,10-dicyanoanthracene, 9-cyanoanthracene in cyclohexane [23]. For these cyano-derivatives, $\Delta G_\mathrm{S}^\mathrm{CT}$ values are positive, so charge-transfer assisted quenching is unlikely and f_Δ^S has been shown to be unity since $(\mathrm{S}_1 \ldots {}^3\Sigma_g^-) > (\mathrm{T}_1 \ldots {}^1\Delta_g)$ and therefore $k_\mathrm{S}^{\mathrm{O}_2} = k_{\mathrm{S}\Delta}$. It is interesting to note that these values of $k_{\mathrm{S}\Delta}$ are similar to the value obtained here for perylene.

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