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Charge Transfer Effects on the Efficiency of Singlet Oxygen Production Following Oxygen Quenching of Excited Singlet and Triplet States of Aromatic Hydrocarbons in Acetonitrile

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Rate constants for quenching by molecular oxygen of excited singlet and triplet states, $k_S^{O_2}$ and $k_T^{O_2}$, respectively, are reported for 12 aromatic hydrocarbons in acetonitrile. Measured values of $k_S^{O_2}$, except in the case of fluoranthene for which $k_S^{O_2} = 6.6 \times 10^9$ dm^3 mol^{-1} s^{-1}, are in the range (2.3−4.3) × 10^{10} dm^3 mol^{-1} s^{-1}, i.e., close to 4.5 × 10^{10} dm^3 mol^{-1} s^{-1}, the average value obtained for k_d, the rate constant for diffusion-controlled reactions of oxygen with aromatic hydrocarbons in acetonitrile. Values of $k_T^{O_2}$ vary from 0.24 to 5.6 × 10^9 dm^3 mol^{-1} s^{-1}. Thus, $k_T^{O_2}/k_d$ was found to be less than one-ninth for 11 compounds. 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, as were the oxidation potentials of the hydrocarbons in acetonitrile. Values of f_Δ^S were shown to be zero within experimental error for eight compounds and in the range of 0.27 ± 0.05 for the other four compounds. Three different methods, which gave good agreement, were used to measure values of f_Δ^T which were found to vary from 0.41 in the case of acenaphthene to 0.85 for anthracene. The fraction of excited singlet states quenched by oxygen which result in triplet states $f_T^{O_2}$ was also measured for all compounds and found to vary from 0.49 to 1.0. 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 in acetonitrile. The reasons for variations in these net quenching rate constants and thus in the fractional efficiencies for quenching by the various quenching pathways are discussed. Quenching of both excited singlet and triplet states by energy transfer and by charge-transfer assisted pathways are established. The logarithm of the net rate constants for quenching of the triplet states without energy transfer to oxygen for 11 of the aromatic hydrocarbons shows a linear dependence on the free energy for full charge transfer from the triplet state, with a slope which indicates that the transition states for this quenching pathway only have about 13.5% charge-transfer character.

Introduction

The ground state of molecular oxygen $O_2(^3\Sigma_g^-)$ is a potent quencher of electronically excited states of molecules.[1−28] Rate constants for quenching by oxygen of excited singlet states in solution $k_S^{O_2}$ are well-known to have high values[2] often approaching the diffusion-controlled limiting rate constant k_d. Murov et al.[2] quote only two values for $k_S^{O_2}$ in acetonitrile these being for 1,4-dicyanonaphthalene and *N*,*N*,*N*′,*N*′-tetramethylbenzidine with $k_S^{O_2}$ equal to 1.3 and 4.0 × 10^{10} dm^3 mol^{-1} s^{-1}, respectively. However, in 1993, Kikuchi et al.[3] demonstrated that $k_S^{O_2}$ values, in acetonitrile as solvent, decrease in the case of four cyanoanthracenes and of five acridium ions, from 16 to 5.3 × 10^9 dm^3 mol^{-1} s^{-1} and from 2.2 to 0.1 × 10^9 dm^3 mol^{-1} s^{-1} as ΔG_S^{CT}, the free energy change for full electron transfer from the first excited singlet state, increases from −51 to 24 kJ mol^{-1} and from −75 to 44 kJ mol^{-1}, respectively. In addition, Sato et al.[4] have measured $k_S^{O_2}$ for nine aromatic hydrocarbons in acetonitrile and in six cases values between 3.2 and 3.7 × 10^{10} dm^3 mol^{-1} s^{-1} were obtained, they have suggested that this corresponds to diffusion-controlled quenching when $\Delta G_S^{CT} < -77$ kJ mol^{-1}. The lowest $k_S^{O_2}$ value these authors observed was 8.2 × 10^9 dm^3 mol^{-1} s^{-1} for oxygen quenching of fluoranthene fluorescence. Recently,[5] we have reported that fluorescence quenching by molecular oxygen of several anthracene derivatives in acetonitrile occurs with $k_S^{O_2}$ values in the range (3−5) × 10^{10} dm^3 mol^{-1} s^{-1} with two exceptions where the rate constants drop to 0.94 × 10^{10} dm^3 mol^{-1} s^{-1} for 9-cyanoanthracene and 0.44 × 10^{10} dm^3 mol^{-1} s^{-1} for 9,10-dicyanoanthracene.

In contrast to the situation concerning $k_S^{O_2}$, there are many rate constants, $k_T^{O_2}$, for triplet state quenching by oxygen in acetonitrile listed in the Handbook of Photochemistry.[2] For reactions between two triplet states, the spin statistical factor is one-ninth for the production of a singlet encounter complex,[6] and in the vast majority of cases, $k_T^{O_2}$ values are less than $k_d/9$ (e.g., taking as an average value $k_d = 4.5 \times 10^{10}$ dm^3 mol^{-1} s^{-1} [see ref 7 and later discussion]). There are three exceptions given in the compilation by Murov et al.[2] where the $k_T^{O_2}$ values are greater than $4k_d/9$. Thus, oxygen quenching of the triplet states of acetone, butanone, and 2-pentanone are reported to be 5.4, 4.3, and 3.2 × 10^{10} dm^3 mol^{-1} s^{-1}, respectively.[8] However the authors[8] who reported these high values stated that they used

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SCHEME 1

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

$$\left.\begin{array}{ll} 2. & {}^1M^* \xrightarrow{k_f} {}^1M + h\nu_f \\ 3. & {}^1M^* \xrightarrow{k_{ic}} {}^1M \\ 4. & {}^1M^* \xrightarrow{k_{isc}} {}^3M^* \end{array}\right\} k_{SD} = k_f + k_{ic} + k_{isc} \qquad \begin{array}{l} \Phi_F^O = k_f / k_{SD} \\ \Phi_T^O = k_{isc} / k_{SD} \end{array}$$

$$\left.\begin{array}{ll} 5. & {}^1M^* + {}^3O_2 \xrightarrow{kS\Delta} {}^3M^* + {}^1O_2^* \\ 6. & {}^1M^* + {}^3O_2 \xrightarrow{kST} {}^3M^* + {}^3O_2 \\ 7. & {}^1M^* + {}^3O_2 \xrightarrow{kSO} \text{Quenching}^a \end{array}\right\} k_S^{O2} = k_{S\Delta} + k_{ST} + k_{SO} \qquad \begin{array}{l} f_\Delta^S = k_{S\Delta} / k_S^{O2} \\ f_T^{O2} = (k_{S\Delta} + k_{ST}) / k_S^{O2} \\ \Phi_F^O / \Phi_F = F^o / F = 1 + k_S^{O2}[O_2] / k_{SD} \\ P_S^{O2} = k_S^{O2}[O_2] / (k_{SD} + k_S^{O2}[O_2]) \\ \quad = (F^o - F) / F^o \end{array}$$

$$8.\quad {}^3M^* \xrightarrow{kTD} {}^1M$$

$$\left.\begin{array}{ll} 9. & {}^3M^* + {}^3O_2 \xrightarrow{kT\Delta} {}^1M + {}^1O_2^* \\ 10. & {}^3M^* + {}^3O_2 \xrightarrow{kTO} \text{Quenching}^a \end{array}\right\} k_T^{O2} = k_{T\Delta} + k_{TO} \qquad \begin{array}{l} f_\Delta^T = k_{T\Delta} / k_T^{O2} \\ P_T^{O2} = k_T^{O2}[O_2] / (k_{TD} + k_T^{O2}[O_2]) \end{array}$$

$$\left.\begin{array}{ll} 11. & {}^1O_2^* \xrightarrow{k\Delta d} {}^3O_2 \\ 12. & {}^1O_2^* \xrightarrow{k\Delta p} {}^3O_2 + h\nu_p \end{array}\right\} k_\Delta = k_{\Delta p} + k_{\Delta d}$$

[a] Step 7 includes all quenching which is not due to catalyzed intersystem crossing, with or without energy transfer to give singlet oxygen, and step10 includes all quenching of the triplet state which does not lead to singlet oxygen. Thus, any quenching reactions, via exciplex formation or not, with or without cage escape to give ions, provided they do not result in $O_2^*(^1\Delta_g)$ or $^3M^*$, are included in steps 7 and 10, as would be any chemical reaction.

oxygen saturated acetonitrile solutions and take the oxygen concentration in acetonitrile as 1.3×10^{-3} mol dm^{-3}. Had they used a value of 9.3×10^{-3} mol dm^{-3} (see ref 2), the values reported would have decreased 7-fold and would all be $<4k_d/9$. We have reported values of $k_T^{O_2}$ for a series of naphthalene[9] and biphenyl[7,10] derivatives in acetonitrile and other solvents and have shown that the rate constants increase as the oxidation potentials decrease and the maximum values observed are $<4k_d/9$ in all solvents.

Oxygen quenching may be accompanied by the transfer of excitation energy to the oxygen molecule, generating directly, or indirectly, through the production of $O_2^*(^1\Sigma_g^+)$, the first excited state of the oxygen molecule $O_2^*(^1\Delta_g)$, which we shall refer to henceforth as singlet oxygen. Singlet oxygen, which has a long lifetime since return to its ground state is spin forbidden, is a highly reactive species and is responsible for oxidative processes in a number of systems.[1] It is well-known that singlet oxygen is produced with varying efficiency as a consequence of quenching of both excited singlet and triplet states. In a compilation[1] of the quantum yields Φ_Δ for the photosensitized formation of the lowest electronically excited state of molecular oxygen in solution, 1400 values are reported for 754 different compounds in a wide range of solvents. However, the fraction of triplet states quenched by oxygen which yield singlet oxygen f_Δ^T and the fraction of excited singlet states quenched by oxygen which yield singlet oxygen, f_Δ^S (see Scheme 1) only had been measured in 357 and 28 cases, respectively, when this compilation was made in 1993. Despite a lot of published data,[1-28] much remains to be done in order to provide a general interpretation to explain the reasons why oxygen quenching of the excited states of certain compounds yield singlet oxygen with high and others with low efficiency. Further information on these fundamental constants should help enhance understanding of the determining parameters. In this paper we report measurements which help to explain why different aromatic hydrocarbons form singlet oxygen with a variety of different efficiencies during oxygen quenching of electronically excited triplet and singlet states in the polar solvent acetonitrile.

The various competing reactions can be understood by considering Scheme 1.

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.,

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

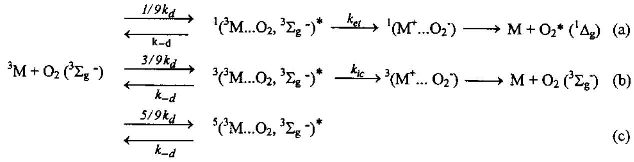
Quenching of the excited singlet state by oxygen leads to a Stern–Volmer relationship between the fluorescence intensities of the sensitizer in the absence and presence of oxygen, F^0 and F, respectively, as given in Scheme 1. The rate constants for quenching of singlet and triplet states by oxygen, $k_S^{O_2}$ and $k_T^{O_2}$, respectively, and f_Δ^T, have been 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.[1-28]

In 1971 Potashnik et al.[11] showed that oxygen quenching of the lowest excited singlet state of eight aromatic hydrocarbons induces intersystem crossing with high yield in toluene but this yield drops when acetonitrile is used as solvent. Thus, the fraction of singlet states quenched by oxygen which yield triplet states, with or without singlet oxygen production, $f_T^{O_2}$ (see Scheme 1) was found to be ≥ 0.9 in all cases with toluene as solvent but decreased with acetonitrile as solvent to give values in the range 0.55 to 0.9. More recently, $f_T^{O_2}$ values for anthracene and eight of its derivatives were measured and found to vary from 0.57 to 0.83 in acetonitrile[5] despite the fact that in cyclohexane these same derivatives have $f_T^{O_2}$ values of unity.[12] Sato et al.[4] also have measured $f_T^{O_2}$ arising following oxygen quenching of the excited singlet states of nine aromatic hydrocarbons in acetonitrile and have found values between 0.36 and 1.0.

Very few groups have reported f_Δ^S values; however, in 1990 McLean et al.[13] 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 zero in all cases except for pyrene and perylene for which values of 0.13 and 0.56, respectively, were reported. The values reported for f_Δ^T varied between 0.31 for benzophenone to 0.79 for protoporphyrin-IX-dimethylester.[13] However, these authors assumed $f_T^{O_2}$ values of unity, as did Usui et al.[14] who reported f_Δ^S and f_Δ^T values for seven aromatic hydrocarbons in cyclohexane. The assumption of $f_T^{O_2}$ values of unity may be justified in these two cases since the solvents used were non polar. The efficiencies of singlet oxygen production from the singlet and triplet states of a series of anthracene derivatives in acetonitrile and cyclohexane were recently reported by us.[5,12] For anthracene and eight of its meso derivatives, the values of f_Δ^S measured in acetonitrile as a solvent are lower than those reported in cyclohexane for the same compounds,[12] and these values vary from 0 to 0.50.

Many more measurements have been made of f_Δ^T and thus much more is known concerning the efficiencies of singlet oxygen production during quenching of triplet states than of singlet states. Recently, the values of $k_T^{O_2}$ and f_Δ^T were reported by us and shown to be inversely correlated for a range of substituted biphenyl,[7,10] naphthalene,[9] and anthracene derivatives[5,12] in acetonitrile, benzene, and cyclohexane. Both $k_T^{O_2}$ 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

SCHEME 2



production increase with the oxidation potential and decrease with increasing solvent polarity. 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[15] have shown a similar dependence is apparent for a much wider range of aromatic compounds in toluene as solvent. Oxygen quenching of triplet states can be interpreted[16] using Scheme 2 based on that originally proposed by Gijzeman et al.[6]

According to Scheme 2 quenching occurs via the singlet and triplet channels (a) and (b) but energy transfer arises only from quenching via the singlet channel. Thus

$$k_T^{O_2} = (k_d/9)[k_{et}/(k_{et} + k_{-d})] + (3k_d/9)[k_{ic}/(k_{ic} + k_{-d})] \tag{2}$$

and

$$f_\Delta^T = (k_d/9)[k_{et}/(k_{et} + k_{-d})]/k_T^{O_2} \tag{3}$$

Equations 4 and 5 define net rate constants $k_{T\Delta}$ and k_{TO} for steps 9 and 10 in Scheme 1 for quenching via the singlet channel (a) and via the triplet channel (b) with and without energy transfer to oxygen, respectively.

$$k_{T\Delta} = k_T^{O_2} f_\Delta^T \tag{4}$$

$$k_{TO} = k_T^{O_2} (1 - f_\Delta^T) \tag{5}$$

To account for $k_T^{O_2}$ values higher than $k_d/9$, Garner and Wilkinson[16] suggested the involvement of charge-transfer complexes in the mechanism of quenching by molecular oxygen and the possibility of intersystem crossing between channels. Recently, Darmanyan et al.[17] have reported that oxygen quenching of the triplet states of several aromatic amines in cyclohexane give $k_{T\Delta}$ values greater than $k_d/9$ and k_{TO} values almost equal to $k_d/3$. These authors propose intersystem crossing from the quintet channel (c) to channel (a) and possibly channel (b) to explain their results.

In this paper we extend our investigations on the factors governing the generation of singlet oxygen during oxygen quenching of both excited singlet and triplet states to various aromatic hydrocarbons in acetonitrile. The compounds under investigations have been selected to have a wide range of energy states and of oxidation potentials to aid with the understanding of the mechanism of quenching by oxygen.

Experimental Section

Materials. Acenaphthene (Aldrich, 99%), anthracene (Sigma 99+%), Biphenyl (Aldrich 99%), chrysene (Aldrich, zone refined, 98%), 1,2,3,4-dibenzanthracene (Koch Light, pure), fluoranthene (Aldrich, 99%), naphthalene (Aldrich, scintillation grade, Gold Label), perylene (Aldrich, 99.5%), phenanthrene (Aldrich, 99.5%), pyrene (Aldrich, 99%), tetracene (Aldrich, 99%), 1-iodopropane (Aldrich, 99%), and acridine (Aldrich, 99%) were all used as received. Triphenylene (Aldrich, 98%) was recrystallized from toluene. Acetonitrile (Aldrich, spectrophotometric grade) was dried by refluxing over calcium hydride.

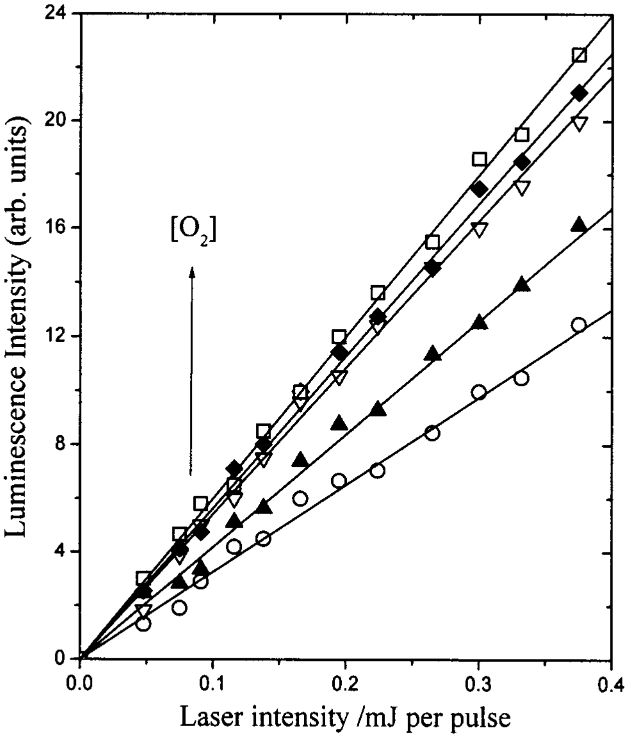


Figure 1. Dependence of the initial luminescence intensity I_0 due to singlet oxygen phosphorescence on the laser fluence following laser excitation at 266 nm of optically matched perylene solutions containing different oxygen concentrations in acetonitrile.

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 266 nm (maximum 23mJ) and at 355 nm (maximum 11mJ), 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 (12 at least) were signal averaged and were fitted using a single-exponential function to yield the luminescence intensity I_o at $t = 0$. The luminescence intensity, I_o 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. Acridine was used as the standard for excitation at both 266 and 355 nm, [$\Phi_\Delta = 0.82$ (ref 25)]. The absorbances of the optically matched solutions were usually 0.30 at 266 or 355 nm. A typical set of results is shown in Figure 1 for perylene in acetonitrile.

The same laser was used as the excitation source for kinetic absorption measurements with a 300 W xenon arc lamp as the analyzing source. Full details of the laser flash photolysis instrument has been given previously.[29] The rate constants $k_T^{O_2}$ for oxygen quenching of the triplet states were determined using eq 6

$$k_{obs} = k_{TD} + k_T^{O_2}[O_2] \qquad (6)$$

where k_{obs} and k_{TD} 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.

The pseudo-first-order decay constant k_{obs} was measured in air-saturated solutions, and the oxygen concentration in air equilibrated acetonitrile[2] was taken to be 1.9×10^{-3} mol dm^{-3}. It has been found that, except for tetracene, none of the compounds investigated showed any photodegradation when subjected to laser photolysis. However, the concentration of tetracene decreases dramatically upon laser excitation and therefore a newly prepared solution was used after each laser exposure.

Kinetic absorption measurements were carried out using dilute, air-equilibrated acetonitrile solutions of the compounds under investigation. Analysis of the transient spectra at times ≥60 ns after lasing demonstrated the lack of formation of cation radicals from any of the aromatic hydrocarbons, although we have previously shown[10] radical cations can be detected using this system following laser photolysis of several of these compounds in the presence of the electron acceptor 9,10-dicyanoanthracene.

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 $k_S^{O_2}$.

Cyclic voltammograms were recorded using an EG&G Princeton Applied Research (PAR) 173 potentiostat with a PAR 175 universal programmer and a PAR 179 digital coulometer. A three-compartment cell was employed with a platinum wire (0.32 cm^2 surface area) working electrode and platinum mesh counter electrode. Electrode potentials were measured and are quoted with respect to a sodium chloride saturated calomel electrode (SSCE) at 25 ± 2 °C. (N.B. 0.005 V less than SCE). No *iR* compensation was employed. Both counter and reference electrodes were separated from the working electrode compartment of the electrochemical cell by glass frits. Platinum working electrodes were pretreated by immersion in concentrated sulfuric acid; anodization, then cathodization, (2 min each at 100 mA in 0.5 mol dm^{-3} sulfuric acid) followed by washing with deionized water, then acetonitrile and finally air-dried. Measurements were carried out in deoxygenated acetonitrile solutions by purging with solvent saturated nitrogen gas. Tetrabutylammonium-perchlorate (0.1 mol dm^{-3}) was used as the supporting electrolyte. The values obtained for the half wave oxidation potential E_M^{OX}, which were comparable with those in the literature,[30] are given in Table 1.

Results and Discussion

The photophysical properties of the aromatic hydrocarbons under investigation are collected in Table 1, which shows that the energy of the lowest excited singlet state (E_{S_1}) covers a wide range from 254 to 391 kJ mol^{-1} and the energy of the lowest excited triplet state (E_{T_1}) ranges even further, i.e., from 123 to 280 kJ mol^{-1}. The energy difference between the lowest excited singlet and triplet states is ≥94 kJ mol^{-1} for most of the compounds with three exceptions, phenanthrene, triphenylene and chrysene, where $E_{S_1} - E_{T_1}$ values are 87, 66, and 91 kJ mol^{-1}, respectively. Since $O_2^*(^1\Delta_g)$ lies 94 kJ mol^{-1} above the ground state, it is unlikely that these three sensitizers 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 nine sensitizers which have $E_{S_1} - E_{T_1}$ and $(E_{T_1}) \geq 94$ kJ mol^{-1}. (Nota bene: For fluoranthene, $E_{S_1} - E_{T_1}$ is ≈ 93 kJ mol^{-1}.) Where E_{T_2} values were not available in the literature, these were determined from measurements of rate constants in benzene for fluorescence quenching by iodopropane k_q^{IP}, and using the empirical relationship between k_q^{IP} and the energy gap $E_{S_1} - E_{T_2}$ as given in ref 31. Values of E_{T_2} obtained in this way are subject to considerable uncertainty.

Values of $f_T^{O_2}$ the fraction of excited singlet states quenched by O_2 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^0 of optically matched solutions of each hydrocarbon in the presence and absence of oxygen respectively using the following equation:[5]

$$\Phi_T^0\left(\frac{A_T^{O_2}}{A_T^0} - \frac{F}{F^0}\right) = f_T^{O_2}\left(1 - \frac{F}{F^0}\right) \qquad (7)$$

Plots according to eq 7 are shown in Figure 2 for naphthalene, biphenyl, and 1,2,3,4-dibenzanthracene. 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, in this case, the triplet absorbance A_T was measured in the presence of 0.05 and 0.07 mol dm^{-3} of iodopropane which quenches perylene fluorescence by catalyzed 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. The following equation, where the subscripts IP and O_2 relate to measurements made in the presence of iodopropane and oxygen, was used to calculate $f_T^{O_2}$ at two different fluorescence quenching ratios.

$$\left(\frac{\Phi_T^0 + (F^0/F) - 1}{A_T(F^0/F)}\right)_{IP} = \left(\frac{\Phi_T^0 + f_T^{O_2}[(F^0/F) - 1)]}{A_T(F^0/F)}\right)_{O_2} \qquad (8)$$

$f_T^{O_2}$ values for all the compounds studied are collected in Table 2.

When the amount of oxygen dissolved in solution is varied so as to affect the amount of fluorescence quenching but always kept high enough such that oxygen quenching of the triplet state is the dominant triplet decay pathway at all the concentrations of dissolved oxygen used, i.e., provided $P_T^{O_2} = 1$ for each oxygen concentration used, then according to Scheme 1, eq 9 will hold. Thus, the measured singlet oxygen quantum yield Φ_Δ, the efficiency of singlet oxygen production from the singlet and triplet states f_Δ^S and f_Δ^T, respectively, the fraction of singlet state quenched by oxygen which yield triplet states $f_T^{O_2}$, the quantum yield of triplet state production in the absence of oxygen Φ_T^0, and the fluorescence intensities in the presence and absence of oxygen F and F^0 are related through the following equation.[1]

$$\Phi_\Delta \frac{F^0}{F} = (f_\Delta^S + f_T^{O_2} f_\Delta^T)\left(\frac{F^0}{F} - 1\right) + \Phi_T^0 f_\Delta^T \qquad (9)$$

Plots of $\Phi_\Delta(F^0/F)$ versus $[(F^0/F)-1]$ give good straight lines as shown in Figures 3a−c. The values obtained for the intercepts $(f_\Delta^T\Phi_T^0)$ and slopes $(f_\Delta^S + f_T^{O_2} f_\Delta^T)$ are collected in Table 2. Combination of the intercepts of the plots shown in Figures 3a−c together with the values of the triplet quantum yields as given in Table 1 allows values of f_Δ^T to be determined. Values

TABLE 1: Photophysical Properties of Unsubstituted Aromatic Hydrocarbons in Acetonitrile. Energies of the Excited Singlet States E_{S_1}(± 2 kJ mol^{-1}), Energies of the Triplet States E_{T_1}(± 2 kJ mol^{-1}), and E_{T_2}(± 10 kJ mol^{-1}), Half-Wave Oxidation Potentials E_M^{OX} (± 0.1 V), Triplet Quantum Yields Φ_T^0, and Lifetimes of the Excited Singlet State τ_S

compound	E_{S_1}/kJ mol^{-1}	E_{T_1} [a]/kJ mol^{-1}	E_{T_2}/kJ mol^{-1}	E_M^{OX}/V vs SCE	τ_S/ns	Φ_T^0 [a]
biphenyl	392	274	<392	1.91	15.9[j]	0.78[k]
naphthalene	384	255	371[b]	1.62	105[a]	0.79[k]
acenaphthene	372	248	358	1.31	46[a]	0.58[a]
phenanthrene	344	257	323[c]	1.59	55.1[j]	0.72[c]
triphenylene	346	280	328[d]	1.68	35[j]	0.89[a]
chrysene	330	239	307[e]	1.45	43.7[j]	0.85[a]
pyrene	322	202	275[c]	1.22	374[j]	0.46[c]
anthracene	319	178	312[c]	1.20	5.8[a]	0.68[c]
1,2,3,4-DBA	318	213	293[f]	1.37	43[a]	0.85[a]
fluoranthene	314	221	268[c]	1.61	46[c]	0.27, 0.25[c]
perylene	273	151	287[g]	0.97	6[a]	0.03[g]
tetracene	253	123	246[h]	0.87[i]	6.4[a]	0.62 ± 0.04[a]

[a] Reference 2. [b] Estimated from ref 39. [c] Reference 4. [d] Reference 40. [e] Reference 14. [f] Reference 31. [g] Reference 41. [h] Reference 42. [i] Reference 43, adjusted for different supporting electrolyte, by comparison with other compounds. [j] Reference 22. [k] Determined from the measurements of fluorescence yields in acetonitrile and ethanol, assuming that $\Phi_f + \Phi_T = 1.0$.

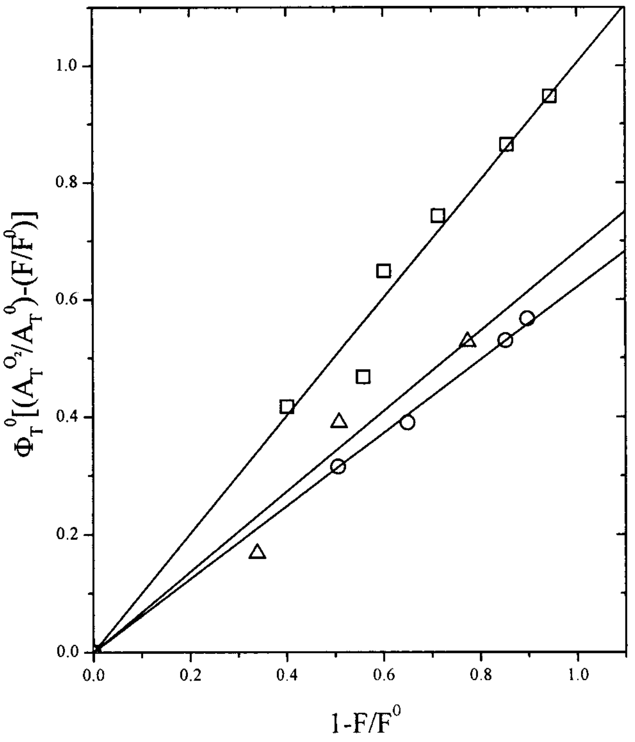


Figure 2. Plots for determining the fractions of excited singlet states S_1 quenched by O_2 which gives triplet states $f_T^{O_2}$ in acetonitrile. (biphenyl (△), naphthalene (○), 1,2,3,4-dibenzanthracene (□)).

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 (see ref 7 for full details of this method). These results are also given in Table 2. Benzophenone was used as triplet donor in the case of phenanthrene and triphenylene, while triplet 2′-acetonaphthone was used to sensitize the production of the triplet states of chrysene, pyrene, 1,2,3,4-dibenzanthracene, 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 mol dm^{-3} iodopropane to completely quench all fluorescence, enabling their triplet 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 from these different techniques and the values obtained are also listed in Table 2. The values of f_Δ^T obtained from the intercept of plots of the type shown in Figure 3 and by these other two techniques agree within experimental error. The error in the intercepts is about 10% with four exceptions those relating to acenaphthene, fluoranthene, perylene, and pyrene where the error is much higher. Errors in the slopes are <10% in all cases. 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 varies from 0 to 0.30. In only four cases, namely, pyrene, fluoranthene, perylene, and tetracene, are the values of f_Δ^S clearly in excess of experimental error (see Table 2).

Values of the rate constants for oxygen quenching of the lowest excited singlet states $k_S^{O_2}$ are given in Table 3. To interpret these results it is interesting to calculate the appropriate values of k_d, the diffusion-controlled rate constants[32] for the studied compounds using eq 10:

$$k_d = 4\pi N(D_M + D_{O_2})(r_M + r_{O_2}) \tag{10}$$

where N is Avogadro's constant, r_M is the radius of the aromatic molecule, values of which were calculated from Le Bas molecular volumes (e.g., see ref 33) as 3.8 ± 0.4 Å, and r_{O_2} is the oxygen radius taken[32] as 0.2 nm. The diffusion coefficient of oxygen in acetonitrile, D_{O_2} has been reported to be 7.12 (± 0.64) × 10^{-5} cm^2 s^{-1} by different groups.[34−35] Diffusion coefficients of the aromatic hydrocarbons have been measured in this work using cyclic voltammetry by following the peak anodic current (i_{p_a}) at different scan speeds. The values obtained of 2.8 ± 0.8 × 10^{-5} cm^2 s^{-1} agree with those in the literature[36] and substitution into eq 10 gives k_d values of 4.5 (±0.5) × 10^{10} dm^3 mol^{-1} s^{-1} in acetonitrile for 10 of these compounds. Kristiansen et al.[22] measured $k_S^{O_2}$ for five of the compounds studied here in acetonitrile reporting values of 4.3 (±0.6) × 10^{10} dm^3 mol^{-1} s^{-1} for biphenyl and $k_S^{O_2}$ = 2.9 (±0.3) × 10^{10} dm^3 mol^{-1} s^{-1} for the other four hydrocarbons. Sato et al.[4] also measured the oxygen quenching rate constant for the lowest excited singlet state of some of these aromatic hydrocarbons in acetonitrile and report values of $k_S^{O_2}$ in the range 3.5 (±0.3) × 10^{10} dm^3 mol^{-1} s^{-1} with the exception of fluoranthene for which they reported a $k_S^{O_2}$ value of 8.2 × 10^9 dm^3 mol^{-1} s^{-1}. The values of $k_S^{O_2}$ reported by Sato et al.[4] are slightly higher than those measured by Kristiansen et al.,[22] probably because of the

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 Equation 9: $f_T^{O_2}$ Is the Fraction of Excited Singlet States Quenched by Oxygen Which Gives Triplet States, and $f_\Delta{}^S$ and $f_\Delta{}^T$ Are the Efficiencies of Singlet Oxygen Production during Oxygen Quenching of the Excited Singlet and Triplet States, Respectively

compound	intercept ($f_\Delta{}^T \Phi_T^0$)	slope ($f_\Delta{}^T f_T^{O_2} + f_\Delta{}^S$)	$f_T^{O_2}$	$f_\Delta{}^{T\,a}$	$f_\Delta{}^T$	$f_\Delta{}^S$
biphenyl	0.40 ± 0.05	0.47 ± 0.02	0.77 ± 0.1	0.51	0.48[b,c]	≤0.09
naphthalene	0.50 ± 0.05	0.49 ± 0.01	0.72 ± 0.1	0.63	0.62[b]	≤0.04
acenaphthene	0.26 ± 0.01	0.27 ± 0.01	0.57 ± 0.2	0.45[f]	0.41[b,d]	≤0.03
phenanthrene	0.33 ± 0.02	0.38 ± 0.02	0.96 ± 0.1	0.46	0.53[b]	0.00 ± 0.05
triphenylene	0.40 ± 0.05	0.49 ± 0.01	1.0 ± 0.1	0.45	0.49[b]	≤0.02
chrysene	0.54 ± 0.05	0.64 ± 0.02	0.90 ± 0.1	0.64	0.76[b]	≤0.01
pyrene	0.38 ± 0.05	0.69 ± 0.01	0.49 ± 0.1	0.83[f]	0.75[b]	0.30 ± 0.05
anthracene[a]	0.61 ±0.05	0.66 ±0.02	0.73 ± 0.2	0.90	0.85[e]	≤0.02
1,2,3,4-DBA	0.66 ± 0.01	0.83 ± 0.01	1.0 ± 0.12	0.78	0.78[b]	0.05 ± 0.05
fluoranthene	0.29 ± 0.02	0.89 ± 0.01	0.65 ± 0.2	1.0[f]	0.82[e]	0.30 ± 0.05
perylene	0.08 ±0.02	0.77 ± 0.01	0.68 ± 0.1	1.0[f]	0.73[b]	0.27 ± 0.05
tetracene	0.30 ± 0.02	0.73 ± 0.01	1.0 ± 0.2	0.48		0.25 ± 0.05

[a] $f_\Delta{}^T$ determined from the values of the intercept and triplet quantum yields, error ± 10% [b] $f_\Delta{}^T$ determined by triplet energy transfer method from a higher ketone, error ± 10% [c] Reference 9. [d] Reference 7. [e] $f_\Delta{}^T$ determined by enhancement of intersystem crossing from the singlet to triplet state by using iodopropane to get $\Phi_T > 0.99$, error ± 10% [f] Error ± 20%

use a low value of 1.7×10^{-3} mol dm^{-3} for the oxygen concentration in air saturated acetonitrile solutions. On the basis of the values calculated in this work, and considering the experimental values,[2,22] which should be $\leq k_d$, we use in the further discussion an average value of k_d for oxygen quenching in acetonitrile of 4.5×10^{10} dm^3 mol^{-1} s^{-1} for all the compounds studied. On the basis of this value, the values of $k_T^{O_2}/k_d$ obtained by us are in the range 0.007 to 0.125, while values of $k_S^{O_2}/k_d$ are much higher, ranging from 0.5 to 0.96 except for fluoranthene, which has a lower value of 0.15.

The rate constants $k_S^{O_2}$ and $k_T^{O_2}$ given in Tables 3 and 4 can be combined with the measured fractional efficiencies to obtain net rate constants for the steps shown in Scheme 1. Thus, the rate constants for steps 5−7in Scheme 1, are given by

$$k_{S\Delta} = k_S^{O_2} f_\Delta^S \tag{11}$$

$$k_{ST} = k_S^{O_2}(f_T^{O_2} - f_\Delta^S) \tag{12}$$

$$k_{SO} = k_S^{O_2}(1 - f_T^{O_2}) \tag{13}$$

where $k_{S\Delta}$ and k_{ST} are the net rate constants for oxygen quenching of excited singlet states which produces the triplet state with and without energy transfer to oxygen, respectively and k_{SO} is the net rate constant for oxygen quenching of excited singlet states by any process which does not catalyze intersystem crossing to the triplet state. Values of $k_{T\Delta}$, k_{TO}, $k_{S\Delta}$, k_{ST}, and k_{SO} evaluated using eqs 4, 5, 11, 12, and 13 are given in Tables 3 and 4.

A good estimate for the energy of charge-transfer states corresponding to the radical ion pair ($M^{+}\cdots O_2{}^{-}$) is given[37] by eq 14:

$$E_{CT} = F(E_M^{OX} - E_{O_2}^{red}) + C \tag{14}$$

where F is the Faraday constant, E_M^{OX} and $E_{O_2}^{red}$ are the half-wave oxidation potential of the sensitizer, and the half-wave reduction potential of $O_2(^3\Sigma_g)$, respectively, with both potentials referred to the same standard state. C depends on the electrostatic interaction energy, which is inversely proportional to the static relative permittivity ϵ_r of the solvent and on the differences in solvation energies of the separate ions and the ion pair. It is well-known that radical cations of aromatic hydrocarbons have limited stability and cyclic voltametric traces are often far from fully reversible. The values obtained for E_M^{OX} are sensitive to conditions (see ref 30 for a detailed discussion). There are many values in the literature for all the compounds studied. It was felt that measuring E_M^{OX} values under identical conditions in our laboratory would give a best set of values for comparison purposes in this study. (Nota bene: Because traces indicated some irreversible behavior, we quote error values of ±100 mV.) As far as the reduction potential of oxygen is concerned, we have used the value of −0.78 V vs SCE as suggested by Mattes and Farid.[30a] This value is based on the average of two values, −0.82 and −0.75 V from refs 38a and 38b, and must therefore also be regarded as subject to a likely error of ±50 mV. The uncertainties in these values can be accommodated in the constant C which is often taken as zero.[3,4,5,7,23] If C in eq 14 is not zero, and values as high as 0.65 eV have been suggested,[38c] the values calculated for E_{CT} are likely to be subject to a constant error. The values of ΔG_S^{CT} and ΔG_T^{CT}, which equal $E_{CT} - E_{S1}$ and $E_{CT} - E_{T1}$, respectively, when taking $C = 0$, given in Tables 3 and 4, demonstrate that electron transfer to oxygen from all the excited singlet states and all but four of the triplet states is exoergic and yet no separated ions are produced. It is apparent that quenching by direct electron transfer to produce separate ions does not compete effectively with encounter/exciplex formation. Figure 4 shows schematically the electronic energy level diagrams for encounter/exciplex complexes of oxygen with the compounds under investigation. It is the relative ordering of, and the probability of nonradiative transitions between, these encounter/exciplex complexes which therefore determines the rates and efficiencies of the various quenching pathways.

Quenching of Excited Triplet States. As far as oxygen quenching of triplet states of these aromatic hydrocarbons is concerned (tetracene excepted), it is clear that in this study we have observed a behavior similar to that found by us previously for biphenyl[7] and naphthalene[9] derivatives, where as ΔG_T^{CT} decreases $k_T^{O_2}$ values increase and f_Δ^T values decrease. With the exception of tetracene, f_Δ^T values are close to unity for compounds for which the charge-transfer states lie above the locally excited triplet states, namely anthracene, fluoranthene, and perylene, whereas compounds where the charge-transfer state lies below the lowest triplet state have f_Δ^T values less than unity. We have therefore employed the equations derived from Scheme 3 which has been developed previously by us[7,10] to fit the experimental data for $k_{T\Delta}$ and k_{TO}.

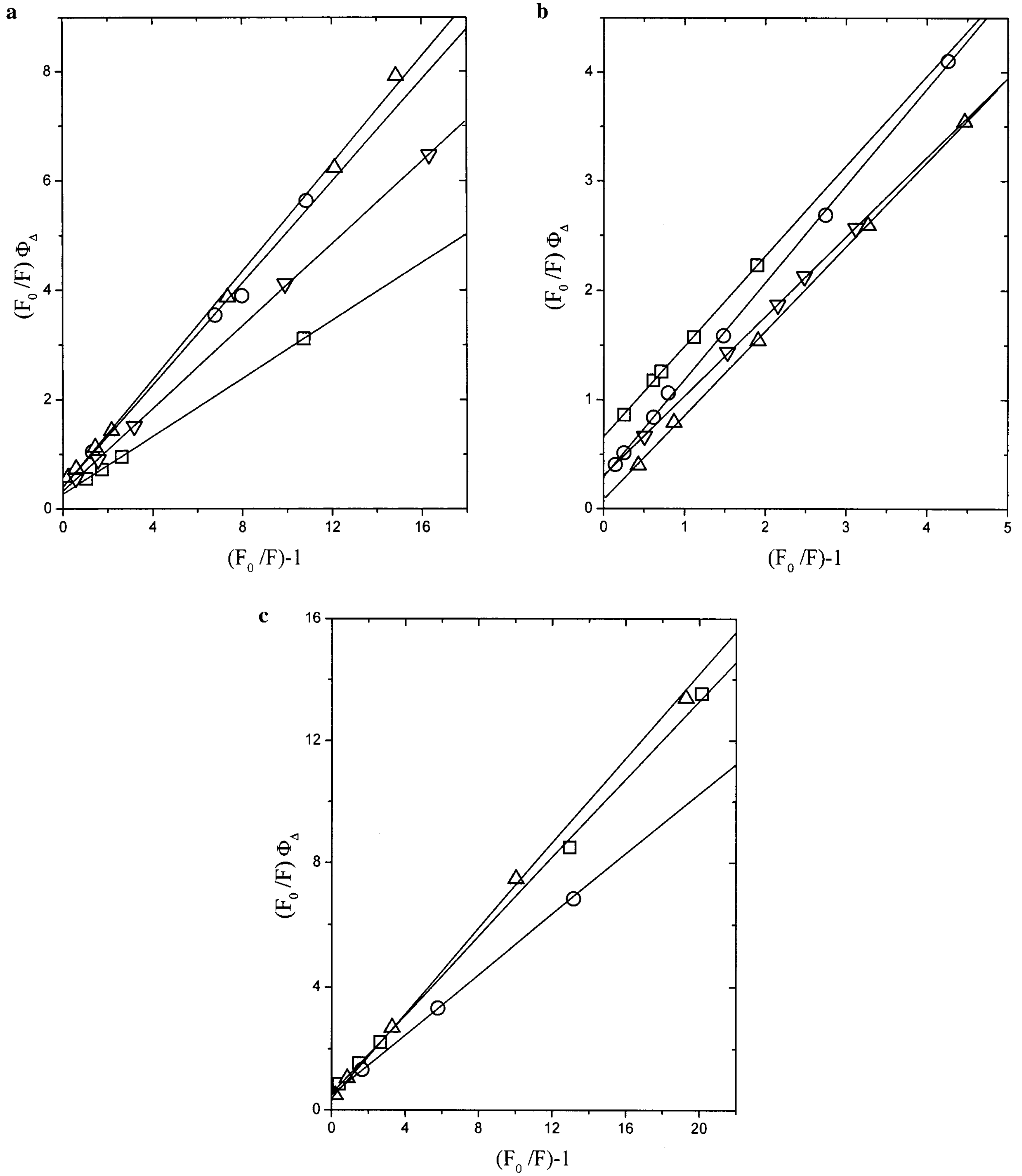


Figure 3. Plots for determining the efficiency of singlet oxygen production from the excited singlet f_Δ^S and triplet states f_Δ^T of aromatic hydrocarbons in acetonitrile. (a) acenaphthene (□), biphenyl (○), triphenylene (△), and phenanthrene (▽). (b) 1,2,3,4-dibenzanthracene (□), fluoranthene (○), perylene (△), and tetracene (▽). (c) chrysene (□), naphthalene (○), and pyrene (△).

In Scheme 3, ^{1,3,5}E and ^{1,3}C are used to represent the encounter and charge-transfer complexes shown in Scheme 2, respectively, and ^{1}P and ^{3}P represent the precursor/encounter complexes $^1(M\cdots O_2^*, {}^1\Delta_g)$ and $^3(M\cdots {}^3O_2, {}^3\Sigma_g^-)$, respectively. Thus, Scheme 3 incorporates Scheme 2 and includes the possibility of direct production of $O_2^*(^1\Delta_g)$ and/or $O_2^*(^1\Sigma_g)$ without passing through the charge-transfer complex ^{1}C, and includes the possibility of intersystem crossing between the different spin multiplets of both the encounter and charge-transfer complexes. (Nota bene: Schemes 2 and 3 are identical when $^1k_\Delta$, and the intersystem crossing rate constants, k_{13} , k_{31} , k_{35} , k_{53} , k_{13}', and k_{31}' are negligibly small.)

Since including intersystem crossing did not improve the fit, we give only the values calculated when all rate constants of intersystem crossing were taken as zero, in which case steady-state treatment of all the reactive intermediates in Scheme 3

TABLE 3: Experimental Values for Rate Constants of Excited Singlet States Quenched by Oxygen $k_S^{O_2}$ [a]

compound	$k_S^{O_2}/10^9$ dm^3 mol^{-1} s^{-1}	$k_{ST}/10^9$ dm^3 mol^{-1} s^{-1}	$k_{S\Delta}/10^9$ dm^3 mol^{-1} s^{-1}	$k_{SO}/10^9$ dm^3 mol^{-1} s^{-1}	ΔG_S^{CT}/kJ mol^{-1}
biphenyl	43 ± 4	29 ± 6	≤3.8	10 ± 2	−133 ± 10
naphthalene	31 ± 3	21 ± 4	≤1.2	9 ± 2	−152 ± 5
acenaphthene	37 ± 4	20 ± 4	≤0.9	16 ± 3	−170 ± 10
phenanthrene	33 ± 3	31 ± 6	≤1.0	≤1.3	−115 ± 5
triphenylene	37 ± 4	36 ± 7	≤0.8	≤1	−109 ± 5
chrysene	33 ± 3	29 ± 6	≤0.4	≤3.3	−115 ± 5
pyrene	29 ± 3	5 ± 1	9 ± 1.0	14.9 ± 3	−129 ± 5
anthracene	30 ± 3	21 ± 4	≤0.7	8.0 ± 2	−128 ± 5
1,2,3,4-DBA	23 ± 2	22 ± 4	≤1.2	≤1	−111 ± 5
fluoranthene	6.6 ± 1	2 ± 0.4	2.0 ± 0.2	2.3 ± 0.4	−83 ± 8
perylene	38 ± 4	16 ± 4	10 ± 2.0	12 ± 3	−105 ± 5
tetracene	42 ± 4	31 ± 6	10 ± 2.0	≤2	−94 ± 10

[a] Derived rate constants (eqs 11−13) for elementary reactions defined in Scheme 1. ΔG_S^{CT} is the free energy changes for electron transfer from the excited singlet states to molecular oxygen ($F(E_M^{OX} - E_{O_2}^{red}) - E_{S_1}$).

TABLE 4: Experimental Values for Rate Constants for Oxygen Quenching of Excited Triplet States $k_T^{O_2}$ [a]

compound	$k_T^{O_2}/10^9$ dm^3 mol^{-1} s^{-1}	$k_{T\Delta}/10^9$ dm^3 mol^{-1} s^{-1}	$k_{TO}/10^9$ dm^3 mol^{-1} s^{-1}	$^1k_\Delta/10^{10}$ s^{-1}	ΔG_T^{CT}/kJ mol^{-1}
biphenyl	2.5 ± 0.2	1.2 ± 0.1 (1.2)	1.2 ± 0.1 (0.7)	2.6	−15 ± 2
naphthalene	2.5 ± 0.2	1.6 ± 0.1 (1.6)	0.9 ± 0.1 (1.0)	3.5	−23 ± 2
acenaphthene	5.6 ± 1.0	2.4 ± 0.2 (2.4)	3.2 ± 0.3 (2.9)	6.1	−46 ± 5
phenanthrene	3.2 ± 0.3	1.6 ± 0.2 (1.6)	1.6 ± 0.2 (1.3)	3.3	−28 ± 3
triphenylene	3.5 ± 0.3	1.6 ± 0.2 (1.6)	1.9 ± 0.2 (2.4)	2.7	−43 ± 4
chrysene	2.0 ± 0.2	1.4 ± 0.1 (1.4)	0.6 ± 0.05 (1.0)	2.8	−24 ± 2
pyrene	2.4 ± 0.2	1.8 ± 0.2 (1.8)	0.5 ± 0.05 (0.5)	5.0	−9 ± 1
anthracene	2.2 ± 0.2	1.9 ± 0.2 (1.9)	0.3 ± 0.03 (0.1)	5.6	13 ± 1
1,2,3,4-DBA	1.4 ± 0.2	1.1 ± 0.1 (1.1)	0.3 ± 0.03 (0.4)	2.2	−6 ± 1
fluoranthene	1.3 ± 0.2	1.2 ± 0.1 (1.2)	0.1 ± 0.01 (0.1)	2.8	10 ± 1
perylene	0.3 ± 0.1	0.2 ± 0.04 (0.2)	0.1 ± 0.02 (<0.01)	0.4	17 ± 2
tetracene	3.5 ± 0.3	1.7 ± 0.2 (1.7)	1.83 ± 0.2 (<0.01)	4.6	36 ± 5

[a] Derived rate constants (eqs 4 and 5) for elementary reactions defined in Scheme 1. Numbers in brackets for $k_{T\Delta}$ and k_{TO} are those obtained by fitting to eqs 15 and 16. Values of $^1k_\Delta$ are those obtained which gave a good fit to the values of $k_{T\Delta}$ using equations derived from Scheme 3. ΔG_T^{CT} is the free energy change for electron transfer from the excited triplet states to molecular oxygen ($F(E_M^{OX} - E_{O_2}^{red}) - E_{T_1}$).

gives[7,10]

$$k_{T\Delta} = \frac{k_d(^1k_T\,^1f_P + k_\Delta)}{9(k_{-d} + {}^1k_T{}^1f_P + k_\Delta)} \tag{15}$$

and

$$k_{TO} = \frac{^3k_d{}^3k_T{}^3f_P}{9(k_{-d} + {}^3k_T{}^3f_P)} \tag{16}$$

where $^1f_p = {}^1k_p/({}^1k_{-T} + {}^1k_P)$ and $^3f_p = {}^3k_p/({}^3k_{-T} + {}^3k_P)$, i.e., ^1f_p and ^3f_p are the fractions of the charge-transfer complexes which dissociate to give $O_2{}^*(^1\Delta_g)$ and $O_2(^3\Sigma_g{}^-)$, respectively.

Using the same or similar parameters as used in our previous fit for biphenyl derivatives,[7] values of $k_{T\Delta}$ and k_{TO} were calculated using Scheme 3 and good fits to the experimental data were found, see Table 4. As in our previous studies[7,10] we use the linear free energy relationship $\Delta G^\ddagger = \alpha + \beta\Delta G_T^{CT}$, as expected from the linear dependence of log k_{TO} on ΔG_T^{CT} shown in Figure 5.

The fits were obtained using the following parameters:

$$k_d = 4.5 \times 10^{10}\ \text{dm}^3\text{mol}^{-1}\text{s}^{-1},\ k_{-d} = 2k_d\ \text{mol dm}^{-3}\ (\text{ref } 6-7),\ {}^1k_p = 2 \times 10^{13}\ \text{s}^{-1},\ {}^3k_p = 2 \times 10^{11}\ \text{s}^{-1}\ {}^1k_T = {}^3k_T = kT/h \exp(-\Delta G^\ddagger/RT),\ {}^1k_{-T} = {}^3k_{-T} = kT/h \exp(-(\Delta G^\ddagger - \Delta G_T^{CT})/RT),\ \text{and}\ \Delta G^\ddagger = 20.5 + 0.135\ \Delta G_T^{CT}$$

(Nota bene: Equally good fits could be obtained using nonzero intersystem crossing rates as high as 2 × 10^{10} s^{-1}; however, good fits were not possible if the intersystem crossing rates were increased to even higher values so that equilibrium between the encounter and charge-transfer complexes ^{1,3,5}E and ^{1,3}C was established. Thus, it is not possible on the basis of these results to establish the extent of intersystem crossing between the spin channels.

It is obvious that the point for tetracene lies far off the line shown in Figure 5 and this requires more detailed investigation. However, we have observed that chemical degradation of tetracene occurs during triplet quenching experiments and we therefore suggest that there is an extra specific chemical step occurring in this case. For all the other aromatic hydrocarbons, no photodegration was observed and a good fit with the experimental data was obtained using the same values for α and β in the expression $\Delta G^\ddagger = \alpha + \beta\Delta G_T^{CT}$ for both singlet and triplet channels. The value of β can be interpreted as representing the fraction of electron transfer,[7] which exists in the transition state for charge-transfer assisted quenching. (Nota bene: The same value of β can be used for both the formation of ^{1}C and ^{3}C for 11 of the hydrocarbons, i.e., excluding tetracene.) The value of 13.5% charge transfer in the transition states for charge-transfer assisted oxygen quenching accounts for the slope of the line shown in Figure 5 being less than $(RT)^{-1}$. An even lower value of 8% charge transfer character was found recently by Darmanyan et al.[17] who studied a series of strong electron donating amines as singlet oxygen sensitizers in cyclohexane and benzene.

In this work no correlation has been found between $k_{T\Delta}$ and ΔG_T^{CT} see Table 4. However, in previous studies of naphthalene and biphenyl derivatives, such a dependence was established and therefore charge-transfer assisted quenching is

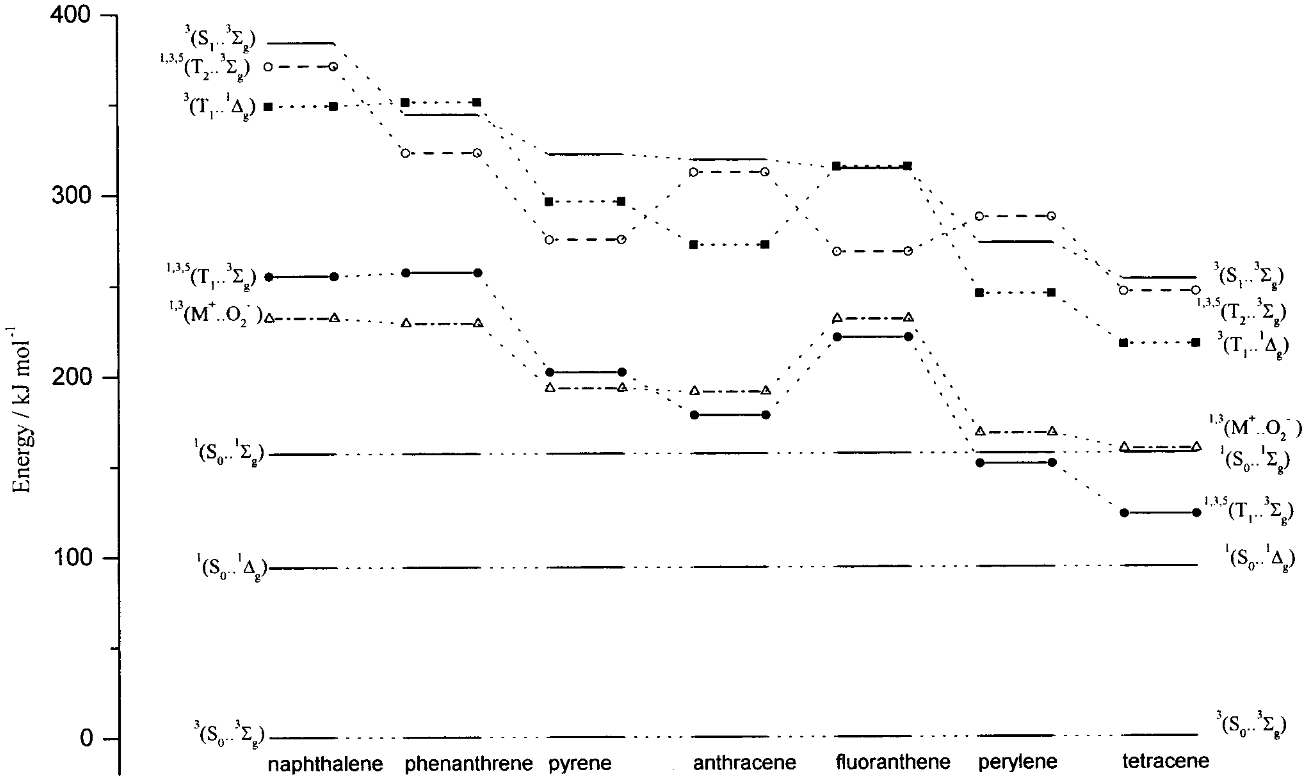
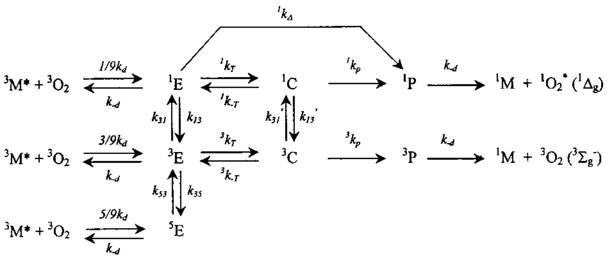


Figure 4. Schematic electronic energy level diagram for encounter complexes ($M\cdots O_2$) formed between unsubstituted aromatic hydrocarbons (M) and molecular oxygen (O_2) in acetonitrile. (Nota bene: The order of energy levels for complexes of (a) biphenyl and acenaphthene are the same as that shown for naphthalene.) (b) triphenylene and chrysene as shown for phenanthrene. (c) 1,2,3,4-dibenzanthracene as shown for pyrene.

SCHEME 3



included here although the main contribution leading to quenching via energy transfer in the singlet channel is according to the fits obtained here via the step in Scheme 3 labeled ${}^{1}k_{\Delta}$. The fitted values of ${}^{1}k_{\Delta}$ are all in the range (2.2−6.1) × 10^{10} s^{-1} except for perylene which yields a value of 4.0 × 10^{9} s^{-1}. The values of these rate constants for nonradiative internal conversion in the encounter complexes $M\cdots O_2$ which we can represent as

$$^{1}(T_1\cdots O_2, {}^{3}\Sigma_g^{-}) \xrightarrow{^{1}k_{\Delta}} {}^{1}(S_0 + {}^{1}O_2({}^{1}\Sigma_g^{+} \text{ and/or } {}^{1}\Delta_g)) \rightarrow M(S_0) + O_2({}^{1}\Delta_g)$$

would be expected to have an energy gap dependence as recently demonstrated by Bodensheim et al.[27] who measured separate oxygen quenching rate constants due to energy transfer to yield both $O_2^*({}^1\Sigma_g^+)$ and $O_2^*({}^1\Delta_g)$ for thirteen organic sensitizers which have triplet energies in the range 140 < E_T < 309 kJ mol^{-1} in carbon tetrachloride solution. It is interesting to note for the series of compounds which we have studied both O_2^*-$({}^1\Sigma_g^+)$ and $O_2^*({}^1\Delta_g)$ are likely to be produced as a result of quenching by energy transfer except in the case of perylene where only $O_2^*({}^1\Delta_g)$ production is energetically possible. (Nota bene: As mentioned earlier, tetracene needs to be considered as an exception since chemical intermediates on the decomposition pathway are probably involved in the production of singlet oxygen in this case.)

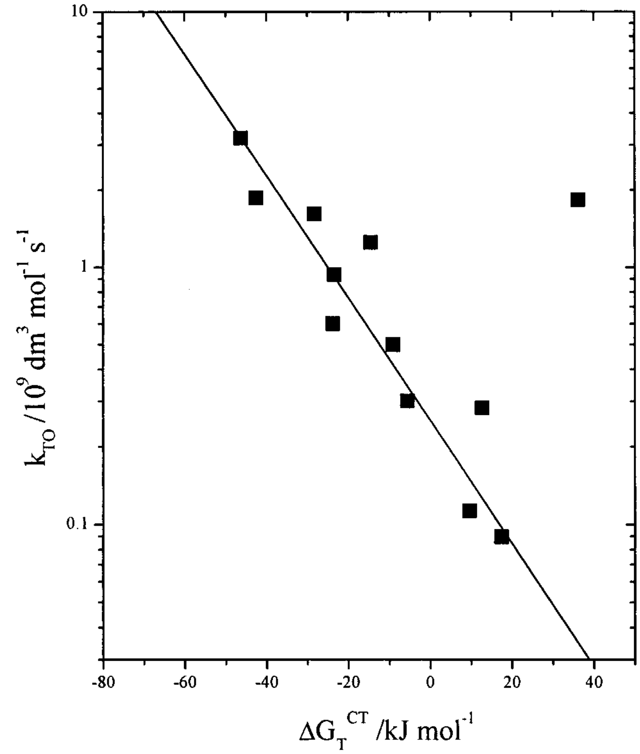


Figure 5. Dependence of the rate constants in acetonitrile for oxygen quenching of triplet states without energy transfer k_{TO} on the free energy change ΔG_T^{CT} see text.

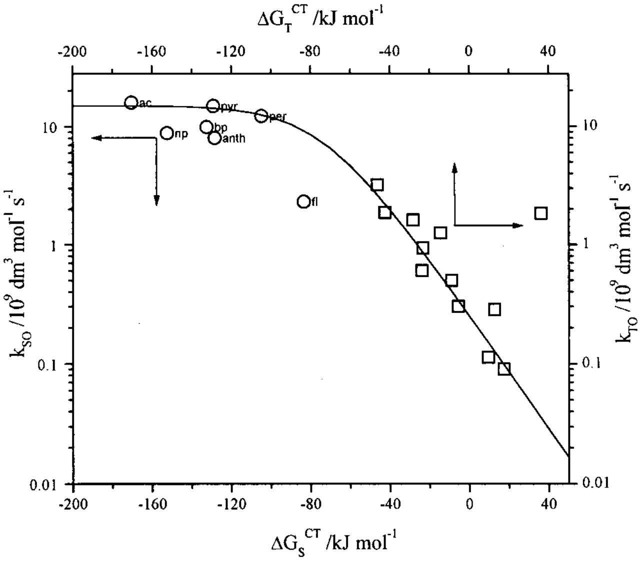
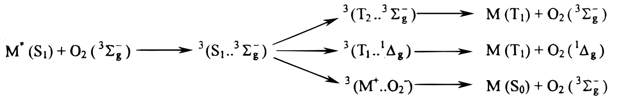


Figure 6. Dependence of the net quenching rate constants in acetonitrile, k_{SO} (○) and k_{TO} (□), defined by eqs 5 and 13, for all compounds under investigation on the corresponding free energy changes ΔG_S^{CT} and ΔG_T^{CT}. (Lables are ac, acenaphthalene; np, naphthalene; bp, biphenyl; pyr, pyrene; anth, anthracene; per, perylene; and fl, fluoranthene.)

Quenching of Excited Singlet States. The dependence of k_{TO} on ΔG_T^{CT} shown in Figure 5 constitutes good evidence for the involvement of charge-transfer interactions in oxygen quenching of triplet states in agreement with several other studies.[7,9,10,15,17,18,27] Despite charge-transfer interactions being the subject of many papers in this area, e.g., see Birks,[36] Chapter 10 and references therein, the importance of charge-transfer interactions in oxygen quenching of excited singlet states is not well established. Potashnik et al.[11] showed that oxygen quenching of the lowest excited singlet state of several aromatic hydrocarbons induces intersystem crossing with yields in acetonitrile as solvent in the range 0.55−0.9. Our previous work with anthracene derivatives[5] and the results reported by Sato et al.[4] together with the values given for $f_T^{O_2}$ in Table 2 confirm that $f_T^{O_2}$ is rarely unity when acetonitrile is used as solvent. Combination of values of $k_S^{O_2}$ and $1 - f_T^{O_2}$ as in eq 13 allows values of k_{SO} the contribution to the rate constant for oxygen quenching of singlet states without the production of triplet states to be evaluated. Figure 6 shows that the dependence of k_{SO} on ΔG_S^{CT} together with our data for the dependence of k_{TO} on ΔG_T^{CT}. Surprisingly the k_{SO} values fall on the best fit curve obtained from the dependence of k_{TO} on ΔG_T^{CT} which is expected to level off as shown for highly negative free energy changes at $k_d/3$ if no intersystem crossings between channels in Scheme 2 or 3 are included. It is important to note that the dependence of the rate constants k_{SO} on ΔG_S^{CT} is slight, and so if the triplet data shown in Figure 6 is ignored, it is quite possible to draw a different curve through the experimental points which could yield a higher plateau rate constant, i.e., approaching 4.5×10^{10} dm^3 mol^{-1} s^{-1} at even more negative values of ΔG_S^{CT}.

As mentioned previously, attempts by us to detect the production of free ions as a result of oxygen quenching of either singlet or triplet states were unsuccessful, even though as can be seen from Tables 3 and 4, ΔG_S^{CT} and ΔG_T^{CT} ranges from 17 to −170 kJ mol^{-1}. Sato et al.[4] also confirm negligible production of ions in their work when $\Delta G_S^{CT} > -140$ kJ mol^{-1}. In fact, they measured the yield of ions produced following oxygen quenching of the singlet excited state of dimethoxynaphthalene where $\Delta G_S^{CT} = -140$ kJ mol^{-1} and found the yield of ion production to be 0.003. These authors have also commented on the fact that they found $f_T^{O_2}$ values decreased to a constant value of about 0.4 when ΔG_S^{CT} is less than −100 kJ mol^{-1}, i.e., this value tends to level off. It has to be born in mind that $k_S^{O_2}$ values are approaching the diffusion limit and the three components k_{SO}, $k_{S\Delta}$, and k_{ST} which are in competition can never be greater than the diffusion-controlled limit.

SCHEME 4



In our previous study of oxygen quenching of the fluorescence of anthracene derivatives in cyclohexane and in acetonitrile[5,12] we demonstrated the crucial importance of internal conversion from the encounter complex $^3(S_1\cdots{}^3\Sigma_g^-)$ and the efficiency of formation of the triplet encounter complex $^3(T_2\cdots{}^3\Sigma_g^-)$ which can undergo internal conversion directly to give $^3(T_1\cdots{}^3\Sigma_g^-)$ by-passing the $^3(T_1\cdots{}^1\Delta_g)$ state which can then dissociate to give $^3M^*(T_1) + O_2(^3\Sigma_g^-)$ without energy transfer. The very low values of f_Δ^S for the first three compounds in Table 2, and for anthracene, can be attributed to the occurrence of these same processes, since the energies of the encounter complexes are in the order $(S_1\cdots{}^3\Sigma_g^-) > (T_2\cdots{}^3\Sigma_g^-) > (T_1\cdots{}^1\Delta_g) > (T_1\cdots{}^3\Sigma_g^-)$. We suggest this ordering of the energy levels within M..O$_2$ complexes explains the high value of $f_T^{O_2}$ for biphenyl, naphthalene, acenaphthene, and anthracene and the large values for k_{ST} which competes effectively with charge-transfer assisted quenching which yields neither T$_1$ nor O$_2$*($^1\Delta_g$). Phenanthrene, triphenylene, and chrysene would be expected to have $f_\Delta^S = 0$ (see Figure 4) since $E_{S_1} - E_{T_1}$ values are less than 94 kJ mol^{-1} and this is confirmed by the experiments. Values of $f_T^{O_2}$ are close to unity and k_{ST} values are similar or slightly higher than for biphenyl, naphthalene, acenaphthene, and anthracene.

The ordering of the energy levels within the M···O$_2$ complexes can also explain why $k_{S\Delta}$ values are high enough in the case of pyrene and fluoranthene to compete with internal conversion to the $(T_2\cdots{}^3\Sigma_g^-)$ complex state since this lies at a lower energy (see Figure 4) yielding f_Δ^S values equal to 0.3. In these cases (see Table 3) $(S_1\cdots{}^3\Sigma_g^-) > (T_1\cdots{}^1\Delta_g) > (T_2\cdots{}^3\Sigma_g^-) > (T^1\cdots{}^3\Sigma_g^-)$. The fact that the energy of the $(T_2\cdots{}^3\Sigma_g^-)$ state lies above that of $(S_1\cdots{}^3\Sigma_g^-)$, in the case of perylene, easily explains why energy transfer becomes likely and f_Δ^S does not equal zero in this case.

It is not possible, from this work, to decide whether internal conversion continues stepwise passing from each higher to each lower encounter/complex state down the energy ladder in competition with dissociation from each encounter/complex state or whether direct competition between radiationless transitions occurs as shown in Scheme 4.

If the order of the energies of the encounter/complex states was the only important parameter determining the relative values of $k_{S\Delta}$, k_{ST}, and k_{SO} with the nearest state being produced most efficiently, 1,2,3,4 dibenzanthracene would be expected to behave like pyrene with f_Δ^S definitely not equal to zero (nota bene: taking errors into account f_Δ^S could be as high as 0.1 in this case), and values for k_{SO} would never become large since the energies of the ion pairs (M$^+\cdots$O$_2^-$) in all cases lie far below E_{S_1}. This is obviously not the case, and it is clear that charge-transfer assisted quenching by oxygen of excited singlet states as does that of triplet states requires a considerable driving force ($\Delta G_S^{CT} < -100$ kJ mol^{-1}) before it occurs with high efficiency. This contrasts with the competing nonradiative transitions where a larger energy gap reduces the probabilities of these competing internal conversions. We suggest that differences in reorganization energies for the three steps shown in Scheme 4 can account for these differences with that for charge-transfer assisted quenching being much greater than for quenching with energy transfer which is probably slightly bigger than that for catalyzed conversion occurring through the $^3(T_2\cdots{}^3\Sigma_g^-)$ state of the complex.

Conclusions

Measurements of the separate efficiencies for oxygen quenching with and without energy transfer and by catalyzed intersystem crossing from S_1 to T_1 combined with measured total quenching rate constants has allowed separate net rate constants for all oxygen quenching pathways of both excited singlet and triplet states to be obtained for the first time. The dependence of the net rate constants for steps 7 and 10 in Scheme 1 (k_{SO} and k_{TO}) on ΔG_S^{CT} and ΔG_T^{CT}, the free energies for formation of the radical ion pair ($M^+\cdots O_2^-$) from singlet and triplet states respectively are shown to be very similar. It is suggested that charge-transfer assisted quenching, which does not lead to the production of free ions even in acetonitrile, is responsible for the dependence on ΔG_S^{CT} and ΔG_T^{CT}. It is noted that these processes only become highly efficient at high driving forces ($\Delta G^{CT} < -100$ kJ mol^{-1}) when the values of k_{SO} and k_{TO} are very similar.

It has been shown that the measured separate rate constants for oxygen quenching of triplet states of all the hydrocarbons (with the exception of tetracene which undergoes chemical degradation) can be fitted to a previously published Scheme 3 using the same fitting parameters if one of the fitting rate constants that for direct energy transfer is allowed to vary. The degree of charge transfer in the transition state for charge-transfer assisted oxygen quenching of the triplet states was found to be about 13.5%.

The relative position of the second excited-state T_2, as has been previously suggested,[5,14] is shown to be crucial in determining whether energy transfer occurs from singlet states even when this is energetically possible. Thus, when $E_{S_1} > E_{T_2} > (E_{T_1} + 94$ kJ mol^{-1}), the energy transfer efficiency f_Δ^S tends to zero; however, when $E_{S_1} > (E_{T_1} + 94$ kJ mol$^{-1}) \gg E_{T_2}$ measurable energy transfer to oxygen from excited singlet states occurs even in acetonitrile.

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