Mechanism of the excited singlet and triplet states quenching by molecular oxygen in acetonitrile

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Abstract

Rate constants for quenching by molecular oxygen of excited singlet and triplet states, k_q^S and k_q^T, respectively, of some aromatic hydrocarbons in acetonitrile are reported. The fraction of excited singlet states quenched by oxygen which result in triplet states, f_T^S, are in the range of 0.25–0.85. 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 0.28 ± 0.05 for 1,2;5,6-dibenzanthracene, pyrene, fluoranthene, 1,11-benzoperylene and perylene while values of f_Δ^T cover the range of 0.25–1.0. 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. Factors governing the production of singlet oxygen with different efficiencies during quenching of both excited singlet and triplet states by oxygen are discussed.
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Keywords: Singlet oxygen; Quenching; Singlet state; Triplet state; Charge transfer; Energy transfer
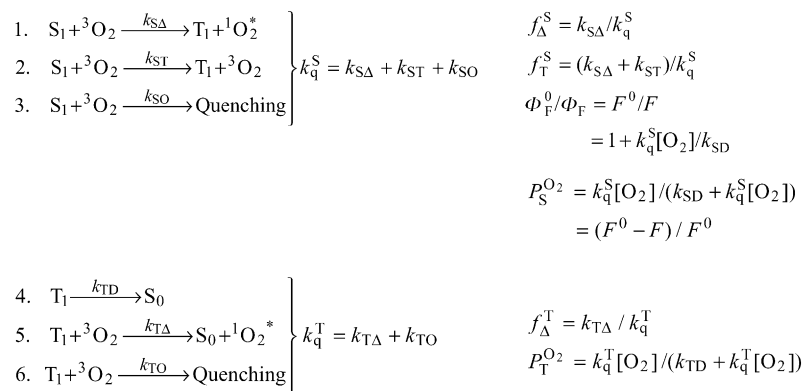
1. Introduction

Oxygen quenching of the electronically excited states [1–4] may be accompanied by the transfer of excitation energy to the oxygen molecule, generating the excited states $O_2^*(^1\Sigma_g^+)$ and/or $O_2^*(^1\Delta_g)$ of the oxygen molecule. The $O_2^*(^1\Delta_g)$ state is usually referred to as singlet oxygen, and has a long lifetime since return to its ground state is spin forbidden. It is a highly reactive species and powerful oxidant in photosensitised oxidations, photodynamic inactivation of viruses and cells, phototherapy for cancer, in photocarcinogenisis, photodegradation of dyes and polymers [2] and blood sterilization [5]. The various processes by which oxygen can interact with excited states can be understood by considering Scheme 1. It is well known that singlet oxygen

is produced with varying efficiency as a consequence of quenching of both excited singlet (S_1) and triplet (T_1) states [1–3]. The quantum yields, Φ_Δ, for the photosensitized formation of the lowest electronically excited state of molecular oxygen in solution have been reported for a large number of compounds in a wide range of solvents [1–4]. However, the fraction of excited singlet states quenched by oxygen which yield singlet oxygen, f_Δ^S and the fraction of the excited singlet state quenched by oxygen to give the triplet state, f_T^S (see Scheme 1) have only been measured in minority of singlet oxygen studies [1,2,6–13]. Despite the large number of studies on the quenching of the excited triplet state by molecular oxygen [1–3,8–55], the fraction of the excited triplet states quenched by oxygen which give singlet oxygen, f_Δ^T, has been reported only in a number of cases [1–3,8–27,29–39,41–50]. It has been shown that both the rate constants for quenching of triplet states by oxygen, k_q^T, and f_Δ^T depend on several factors including oxidation potential, E_{ox}, of the sensitizer [10,11,14–27,38], energy of the triplet state, E_T [10,11,14,15,28,29], nature

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1. $S_1 + {}^3O_2 \xrightarrow{k_{S\Delta}} T_1 + {}^1O_2^*$
2. $S_1 + {}^3O_2 \xrightarrow{k_{ST}} T_1 + {}^3O_2$ $\left.\vphantom{\begin{matrix}1\\2\\3\end{matrix}}\right\} k_q^S = k_{S\Delta} + k_{ST} + k_{SO}$
3. $S_1 + {}^3O_2 \xrightarrow{k_{SO}} \text{Quenching}$

$f_\Delta^S = k_{S\Delta}/k_q^S$

$f_T^S = (k_{S\Delta} + k_{ST})/k_q^S$

$\Phi_F^0/\Phi_F = F^0/F$

$\quad = 1 + k_q^S[O_2]/k_{SD}$

$P_S^{O_2} = k_q^S[O_2]/(k_{SD} + k_q^S[O_2])$

$\quad = (F^0 - F)/F^0$

4. $T_1 \xrightarrow{k_{TD}} S_0$
5. $T_1 + {}^3O_2 \xrightarrow{k_{T\Delta}} S_0 + {}^1O_2^*$ $\left.\vphantom{\begin{matrix}4\\5\\6\end{matrix}}\right\} k_q^T = k_{T\Delta} + k_{TO}$
6. $T_1 + {}^3O_2 \xrightarrow{k_{TO}} \text{Quenching}$

$f_\Delta^T = k_{T\Delta}/k_q^T$

$P_T^{O_2} = k_q^T[O_2]/(k_{TD} + k_q^T[O_2])$

Scheme 1.

of the triplet state [14,26,29–55] and polarity of the solvent [9,16,19,20,22,24].

In Scheme 1, steps 1 and 5 include direct production of $O_2^*({}^1\Delta_g)$ from oxygen quenching as well as $O_2^*({}^1\Delta_g)$ formed from any $O_2^*({}^1\Sigma_g^-)$ formed initially. Step 3 includes all quenching, which is not due to catalyzed intersystem crossing, with or without energy transfer, and step 6 includes all quenching of the triplet state which does not lead to singlet oxygen production.

Rate constants for quenching by oxygen of excited singlet states in solution, k_q^S, are well known to have values often approaching the diffusion controlled limiting rate constant, k_d [56]. Kristiansen et al. [57] measured k_q^S for some aromatic hydrocarbons in acetonitrile and reported values of $4.3(\pm0.6) \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ for biphenyl and $k_q^S = 2.9(\pm0.3) \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ for other hydrocarbons. Kikuchi et al. [58] demonstrated that k_q^S values decrease in the case of four cyanoanthracenes and five acridium ions, from 16 to 5.3×10^9 and from 2.2 to $0.1 \times 10^9\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ as ΔG_S^{CT}, the free energy change for full electron transfer from the first excited singlet state, increases from -51 to 24 and from -75 to $44\,\text{kJ}\,\text{mol}^{-1}$, respectively, in acetonitrile. In addition, Sato et al. [7] measured k_q^S for nine aromatic hydrocarbons in acetonitrile and in six cases values between 3.2 and $3.7 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ were obtained; they have suggested that this corresponds to diffusion controlled quenching when $\Delta G_S^{CT} < -77\,\text{kJ}\,\text{mol}^{-1}$. The lowest k_q^S value these authors observed was $8.2 \times 10^9\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ for oxygen quenching of fluoranthene fluorescence. Olea and Wilkinson [9] have reported that fluorescence quenching by molecular oxygen of several anthracene derivatives in acetonitrile occurs with k_q^S values in the range $(3–5) \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ with two exceptions, where the rate constants drop to $0.94 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ for 9-cyanoanthracene and $0.44 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ for 9,10-dicyanoanthracene.

Recently in acetonitrile [11] we have reported values for k_q^S in the range $(2.3–3.8) \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ for a series of aromatic hydrocarbons. A higher value of $4.3 \times 10^{10}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ is reported for biphenyl, which is equal to the calculated value of the diffusion controlled rate constant, k_d, while a lower value of $6.6 \times 10^9\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ is reported for fluoranthene in acetonitrile.
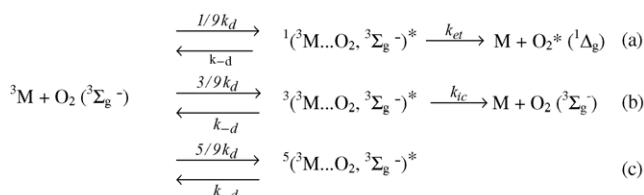
The mechanism of the excited triplet state quenched by oxygen was first described by Gijzeman et al. [28] and is shown in Scheme 2. According to Scheme 2, quenching occurs via the singlet and triplet channels (a) and (b) but energy transfer arises only from quenching via the singlet channel. Thus

$$k_q^T = (k_d/9)[k_{et}/(k_{et} + k_{-d})] + (3k_d/9)[k_{ic}/(k_{ic} + k_{-d})] \quad (1)$$

and

$$f_\Delta^T = (k_d/9)[k_{et}/(k_{et} + k_{-d})]/k_q^T. \quad (2)$$

According to Scheme 2, the efficiency of singlet oxygen generation from the triplet state, f_Δ^T, would be 1.0 and quenching rate constant $k_q^T \leq k_d/9$ if only the singlet channel was involved and f_Δ^T would approach 0.25 with $k_q^T \leq 4k_d/9$ if the singlet and the triplet channels were both involved equally. However, neither of these limiting cases has been observed even though a large number of compounds have been studied {see for example Refs. [1–3] and cited references therein}. For example, for a series of biphenyl and naphthanlene derivatives, some compounds showing quenching rate constants $< k_d/9$ show observed f_Δ^T values far from unity [10,11,16,17,20]. Values of $k_q^T > 4k_d/9$ are also reported in few cases, showing that if the quenching mechanism is as described in Scheme 2 then the quintet encounter complex must also contribute to the overall quenching mechanism [59–61]. In this paper we are extending our investigations into the factors governing the generation of singlet oxygen during oxygen quenching

${}^3M + O_2\,({}^3\Sigma_g^-)$

$\xrightarrow[k_{-d}]{1/9 k_d}$ ${}^1({}^3M\cdots O_2, {}^3\Sigma_g^-)^* \xrightarrow{k_{et}} M + O_2^*\,({}^1\Delta_g)$ (a)

$\xrightarrow[k_{-d}]{3/9 k_d}$ ${}^3({}^3M\cdots O_2, {}^3\Sigma_g^-)^* \xrightarrow{k_{ic}} M + O_2\,({}^3\Sigma_g^-)$ (b)

$\xrightarrow[k_{-d}]{5/9 k_d}$ ${}^5({}^3M\cdots O_2, {}^3\Sigma_g^-)^*$ (c)

Scheme 2.

of both excited singlet and triplet states in acetonitrile to include more compounds that cover a wider range of the energies of the excited states, and also a wide range of oxidation potentials to aid with understanding of the mechanism of excited states quenching by oxygen. The mechanism of the excited singlet states quenching by oxygen and factors that govern the values of f_T^S and f_Δ^S and other parameters are studied. Dependence of these parameters on the oxidation potential and on the energy of the excited states were investigated.

2. Experimental

Cyanophenanthrene (Aldrich, 97%) was recrystallized from ehthanol. 1,2;5,6-Dibenzanthracene (Aldrich, 97%), were double recrystallized from cyclohexane. 2,6-Dimethoxynaphthalene (Aldrich, 99%) and 1,2-benzanthracene (Aldrich, 99%) were used as received. Acenaphthene (Aldrich, 99%), anthracene (Sigma 99+%), fluoranthene (Aldrich, 99%), naphthalene (Aldrich, scintillation grade, Gold Label), perylene (Aldrich, 99.5%), phenanthrene (Aldrich, 99.5%), pyrene (Aldrich, 99%), and acridine (Aldrich, 99%) were all used as received. Acetonitrile (Aldrich, spectrophotometric grade) was dried by refluxing over calcium hydride.

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 23 mJ) and at 355 nm (maximum 11 mJ), respectively. The laser energies employed during Φ_Δ measurements did not exceed 0.5 mJ pulse^{-1}. Time resolved singlet oxygen luminescence (1270 nm) was detected using a liquid nitrogen cooled germanium photodiode detector (EO-980P North Coast Scientific).

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. 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_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. Acridine was used as the standard for excitation at both 266 and 355 nm ($\Phi_\Delta = 0.82$ [62]). The absorbances of the optically matched solutions were usually 0.30 at 266 or 355 nm.

The same laser was used as the excitation source for kinetic absorption measurements with a 300 W xenon arc lamp as the analysing source. The rate constants k_q^T for oxygen quenching of the triplet states were determined using Eq. (3)

$$k_{obs} = k_{TD} + k_q^T[O_2] \tag{3}$$

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 [56] was taken to be 1.9×10^{-3} mol dm^{-3}.

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_q^S.

The half-wave oxidation potentials were measured by cyclic voltammetry in acetonitrile versus SCE as previously described [16]. Some data from our previous publication [11] are reproduced and included here. Data obtained were within the experimental error reported and therefore uncertainty reduced to 10%.

3. 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 273 to 384 kJ mol^{-1} and the energy of the lowest excited triplet state E_{T_1} ranges from 151 to 261 kJ mol^{-1}. The half-wave oxidation potentials, E_{ox} covers a range of 0.97–1.92 V versus SCE.

Values for the fraction of excited singlet states quenched by molecular oxygen which give rise to triplet states, f_T^S, can be obtained from the measured ratios of the fluorescence intensities in the presence and absence of oxygen, F and F^0, and of the triplet–triplet absorbances at time $t = 0$ in the presence and absence of oxygen, A_T and A_T^0, respectively, of optically matched solutions of each hydrocarbon using the following equation [2,6]

$$\Phi_T^0 \left(\frac{A_T}{A_T^0} - \frac{F}{F^0} \right) = f_T^S \left(1 - \frac{F}{F^0} \right) \tag{4}$$

Data obtained for f_T^S from this equation are listed in Table 1.

In order to measure the fraction of the excited singlet states quenched by oxygen to give singlet oxygen, f_Δ^S, 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. Thus the measured singlet oxygen quantum yield Φ_Δ, the efficiencies of singlet oxygen production

Table 1
Photophysical properties of unsubstituted aromatic hydrocarbons in acetonitrile

Compound	E_{S_1} (kJ mol^{-1})	E_{T_1} (kJ mol^{-1})	E_{T_2} (kJ mol^{-1})	E_{ox} (V) vs. SCE	τ_s (ns)	Φ_T^0	k_q^S (×10^{10} dm^3 mol^{-1} s^{-1})	k_q^T (×10^9 dm^3 mol^{-1} s^{-1})	f_T^S	f_Δ^T	f_Δ^S
Naphthalene[11]	384	255	371	1.62	105	0.79	3.1	2.5	0.72 ± 0.10	0.62 ± 0.06	0.04 ± 0.04
Acenaphthalene[11]	372	248	358	1.31	46	0.58	3.7	5.6	0.57 ± 0.06	0.45 ± 0.04	0.03 ± 0.03
Phenanthrene[11]	345	260	323	1.59	55.1	0.72	3.3	3.2	0.96 ± 0.10	0.50 ± 0.05	0.00
2,6-Dimethoxynaphthalene	340	261	–	1.13	10.7[7]	0.95[24]	3.3	9.6	0.25 ± 0.03	0.25 ± 0.02	0.00
1,2;5,6-Dibenzoanthracene	337	219	279[7]	1.39	30.6[7]	0.84[7]	2.9	1.9	0.56 ± 0.06	0.86 ± 0.08	0.28 ± 0.03
9-Cyanophenanthrene	330	243	308[7]	1.92	21.6[7]	0.68[7]	2.3	1.6	0.85 ± 0.10	0.80 ± 0.08	0.04 ± 0.04
Pyrene[11]	322	203	275	1.22	374	0.46	3.1	2.1	0.49 ± 0.05	0.79 ± 0.08	0.30 ± 0.03
Anthracene[11]	319	178	312	1.20	5.8	0.68	3.0	2.2	0.73 ± 0.10	0.87 ± 0.08	0.00
Fluoranthene[11]	315	221	268	1.61	46	0.25	0.66	1.3	0.65 ± 0.07	0.91 ± 0.10	0.30 ± 0.03
1,2-Benzanthracene	311	198	292[7]	1.31	42.1[7]	0.48[7]	3.1	1.9	0.79 ± 0.10	0.90 ± 0.10	0.00
1,11-Benzoperylene	305	194	260[7]	1.03	127[7]	0.29[7]	2.9	1.9	0.36 ± 0.04	0.90 ± 0.10	0.30 ± 0.03
Perylene[11]	273	151	287	0.97	6	0.03	3.8	0.3	0.68 ± 0.10	1.00 ± 0.10	0.27 ± 0.03

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_{ox} (± 0.1 V), lifetimes of the excited singlet state, τ_s, the triplet quantum yields, Φ_T^0 and experimental values for rate constants of excited singlet and triplet states quenched by oxygen, k_q^S and k_q^T respectively and fraction of the excited singlet state quenched by oxygen to give triplet state, f_T^S, or to give singlet oxygen f_Δ^S, and the fraction of the excited triplet state quenched by oxygen to give singlet oxygen, f_Δ^T.

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^S, 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: [2]:

$$\Phi_\Delta \frac{F^0}{F} = (f_\Delta^S + f_T^S f_\Delta^T)\left(\frac{F^0}{F} - 1\right) + \Phi_T^0 f_\Delta^T \qquad (5)$$

Plots of $\Phi_\Delta(F^0/F)$ versus $[(F^0/F) - 1]$ according to Eq. (5), give good straight lines with intercept of $(\Phi_T^0 f_\Delta^T)$ and slope of $(f_\Delta^S + f_T^S f_\Delta^T)$. Combination of the intercepts with the values of the triplet quantum yields as given in Table 1 allows values of f_Δ^T to be determined. Substitution of the obtained values of f_Δ^T and values of f_T^S (Eq. (4)) into the slope of Eq. (5) allows for the determination of f_Δ^S. Data of f_Δ^T, f_T^S and f_Δ^S are listed also in Table 1.

The measured fractional efficiencies f_Δ^S, f_Δ^T and f_T^S can be combined with the quenching rate constants k_q^S and k_q^T to obtain net rate constants for the steps shown in Scheme 1. Thus the rate constants for steps 1–3 in Scheme 1, are given by:

$$k_{S\Delta} = k_q^S f_\Delta^S \qquad (6)$$

$$k_{ST} = k_q^S (f_T^S - f_\Delta^S) \qquad (7)$$

$$k_{SO} = k_q^S (1 - f_T^S) \qquad (8)$$

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} the net rate constant for oxygen quenching of excited singlet states by any process which does not catalyse intersystem crossing to the triplet state.

Eqs. (9) and (10) define net rate constants, $k_{T\Delta}$ and k_{TO} for steps 5 and 6 in Scheme 1 for quenching via the singlet channel (a) and via the triplet channel (b) (Scheme 2) with

and without energy transfer to oxygen, respectively:

$$k_{T\Delta} = k_q^T f_\Delta^T \qquad (9)$$

$$k_{TO} = k_q^T (1 - f_\Delta^T) \qquad (10)$$

Values of $k_{T\Delta}$, k_{TO} obtained from Eqs. (9) and (10) together with values of $k_{S\Delta}$, k_{ST} and k_{SO} evaluated using Eqs. (6)–(8) are given in Table 2.

A good estimate for the energy of charge-transfer states corresponding to the radical ion pair ($M^+..O_2^-$) is given [63] by Eq. (11):

$$E_{CT} = F(E_M^{OX} - E_{O_2}^{red}) + C \qquad (11)$$

where F is the Faraday constant, E_M^{OX} and $E_{O_2}^{red}$ 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. The value of -0.78 V versus SCE for $E_{O_2}^{red}$ is used [64] to calculate E_{CT}. 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. The values of the free energy changes (ΔG_S^{CT} and ΔG_T^{CT}) to form ion pairs from excited singlet and triplet states with energy E_{S_1} and E_{T_1}, are calculated to be $E_{CT} - E_{S_1}$ and $E_{CT} - E_{T_1}$, respectively, when taking $C=0$.

3.1. Quenching of the excited triplet states

Dependence of the rate constant for quenching of triplet state by oxygen, k_q^T, and the efficiency of singlet oxygen, $O_2^*(^1\Delta_g)$, production, f_Δ^T, on the oxidation potential of the aromatic hydrocarbon does not show any correlation (Table 1) on contrast to those reported previously by ourselves and others for different series of aromatic hydrocarbons. Similarly, dependence of the rate constants for quenching by oxygen of excited triplet states, k_q^T on the triplet state energy is still vague, while the dependence of the efficiency of singlet oxygen production on the energy of the triplet state shows some

Table 2
The free energy changes for electron transfer from the excited triplet and singlet states to molecular oxygen ΔG_T^{CT} and ΔG_S^{CT} (see text) and the derived rate constants (Eqs. (6)–(10)) for elementary reactions defined in Scheme 1

Compound	ΔG_T^{CT} (kJ mol^{-1})	$k_{T\Delta}$ ($\times 10^9$ dm^3 mol^{-1} s^{-1})	k_{TO} ($\times 10^9$ dm^3 mol^{-1} s^{-1})	ΔG_S^{CT} (kJ mol^{-1})	$k_{S\Delta}$ ($\times 10^{10}$ dm^3 mol^{-1} s^{-1})	k_{ST} ($\times 10^{10}$ dm^3 mol^{-1} s^{-1})	k_{SO} ($\times 10^{10}$ dm^3 mol^{-1} s^{-1})
Naphthalene[11]	−23.4	1.55	0.95	−152	0	2.23	0.87
Acenaphthalene[11]	−46.3	2.52	3.08	−170	0	2.11	1.59
Phenanthrene[11]	−30.9	1.60	1.60	−116	0	3.18	0.13
2,6-Dimethoxynaphthalene	−76.2	2.40	7.20	−155	0	0.83	2.48
1,2;5,6-Dibenzoanthracene	−9.7	1.63	0.27	−94	0.80	0.80	1.26
9-Cyanophenanthrene	17.4	1.28	0.32	−74	0	1.98	0.35
Pyrene[11]	−8.7	1.66	0.44	−128	0.94	0.59	1.60
Anthracene[11]	13.0	1.91	0.29	−128	0	2.19	0.81
Fluoranthene[11]	10.6	1.18	0.18	−83	0.20	0.23	0.23
1,2-Benzanthracene	3.9	1.71	0.19	−109	0	2.47	0.66
1,11-Benzoperylene	−19.3	1.71	0.19	−130	0.87	0.17	1.83
Perylene[11]	17.8	0.30	0.00	−104	1.03	1.56	1.22

Fig. 1. Dependence of the rate constant for quenching of triplet state by oxygen, k_q^T (□), and the efficiency of singlet oxygen, $O_2^*(^1\Sigma_g^+)$, production, f_Δ^T (●), on the free energy change from the triplet state ΔG_T^{CT}.

Fig. 2. Dependence of $^3k_T^{\ 3}f_P/k_{-d}$ according to Eq. (15) on the free energy change ΔG_T^{CT} in acetonitrile for the current set of compounds (●), for the rest of previously reported unsubstituted aromatic hydrocarbons (○) [11], for biphenyl derivatives (△) [16] and naphthalene derivatives (□) [20] in acetonitrile.

scatter. Dependence of k_q^T and f_Δ^T on the oxidation potential or on the energy of the triplet state is best observed when only one parameter is variable while other variables are kept approximately constant [14–17,19–26]. However, Fig. 1 shows that k_q^T decreases while the efficiency of singlet oxygen production, $O_2^*(^1\Delta_g)$ production, f_Δ^T, increases as the free energy change, ΔG_T^{CT}, increases. The dependence of k_q^T and f_Δ^T on ΔG_T^{CT} is not dissimilar to those reported previously by us (see for example Refs. [16,17,20,21]). Values of k_q^T are $<1/9k_d$ and f_Δ^T values are in the range 0.50–1.0 for all compounds with two exceptions: these are 2,6-dimethoxynaphthalene and acenaphthene where $1/9k_d < k_q^T < 4/9k_d$ and f_Δ^T values are 0.25 and 0.45, respectively. It can be seen (Table 1) that f_Δ^T values are approaching the range expected according to Scheme 2 while k_q^T values are still well below $4/9k_d$ ($k_d = 4.3 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) for two of the compounds and lower than $1/9k_d$ for the rest of compounds.

In 1977 Garner and Wilkinson [65] suggested the involvement of charge transfer complexes and the possibility of intersystem crossing between the various quenching channels in the mechanism of quenching by molecular oxygen. Recently, we have proposed competition between non-charge transfer assisted energy transfer (i.e. also including the step labelled $^1k_\Delta$ in Scheme 3) and charge transfer assisted quenching with

and without energy transfer [16,17], further evidence for the occurrence of which has recently been obtained by Schmidt and co-workers [14,19]. Steady state treatment of all the reactive intermediates in Scheme 3, assuming all intersystem crossing steps between the encounter complexes and charge transfer complexes are negligible, gives [11]:

$$k_{T\Delta} = k_d(^1k_T^{\ 1}f_P + {}^1k_\Delta)/9(k_{-d} + {}^1k_T^{\ 1}f_P + {}^1k_\Delta) \qquad (12)$$

$$k_{TO} = 3k_d^{\ 3}k_T^{\ 3}f_P/9(k_{-d} + {}^3k_T^{\ 3}f_P) \qquad (13)$$

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 dissociates to give $O_2^*(^1\Delta_g)$ and $O_2(^3\Sigma_g^-)$, respectively. When ^1f_P is zero, i.e., when there is no charge transfer assisted quenching, $k_{T\Delta} = k_{T\Delta}^{\Delta E}$ which is given by

$$k_{T\Delta}^{\Delta E} = k_d^{\ 1}k_\Delta/9(k_{-d} + {}^1k_\Delta) \qquad (14)$$

Rearrangement of Eq. (13) gives

$$\frac{^3k_T^{\ 3}f_P}{k_{-d}} = \frac{3k_{TO}}{k_d - 3k_{TO}} \qquad (15)$$

Dependence of $^3k_T^{\ 3}f_P/k_{-d}$ on the free energy change from the excited triplet state ΔG_T^{CT} (Fig. 2) gives a slope of -0.019 ± 0.001. This value is about 11% of the expected slope of full electron transfer quenching of RT^{-1}. Therefore,

Scheme 3.

partial charge transfer participation of about 11% is expected to take place in the quenching of the triplet states by oxygen in acetonitrile, which is not far from what we suggested before for different series of compounds which are also included in the figure for comparison [16,17,20,21]. Inclusion of values for biphenyl [16] and naphthalene derivatives [20] together with un-substituted aromatic hydrocarbons [11] in acetonitrile shows scatter as shown in Fig. 2. Such scatter between different series of compounds point to the involvement of other parameters in the quenching of the excited triplet state by oxygen like molecular parameters [1] which needs further investigations. Inclusion of non-zero intersystem crossing rates as high as $10^{10}\,s^{-1}$ did not change the fit very much as was observed by us previously [16]. However, using higher values for the intersystem crossing rates so that equilibrium between the encounter complexes, $^{1,3,5}(^3M..O_2, {}^3\Sigma_g^-)$, and charge transfer complexes, $^{1,3}(M^{\delta+}..O_2^{\delta-})$, is established did not result in good fits and subsequently the extent of intersystem crossing between the intermediate complexes is not established and still need further investigations.

It is worth mentioning that an alternative kinetic scheme to Scheme 3 is given by Schmidt and co-workers [14,15,18,21]. According to Scheme 3, the ground state molecular oxygen is formed through the triplet channel in the sequence $^3(^3M..O_2, {}^3\Sigma_g^-) \rightarrow {}^3(M^{\delta+}..O_2^{\delta-}) \rightarrow {}^3(M..^3O_2, {}^3\Sigma_g^-)$ with rate constant of $1/3k_d$, and/or through the singlet channel with intersystem crossings between the encounter complexes or charge transfer complexes with quenching rate constant $\leq 1/9k_d$. Whereas, $O_2^*(^1\Delta_g)$ is formed via $^1(^3M..O_2, {}^3\Sigma_g^-) \rightarrow {}^1(M..O_2^*, {}^1\Delta_g)$ and/or the charge transfer assisted energy transfer via $^1(^3M..O_2, {}^3\Sigma_g^-) \rightarrow {}^1(M^{\delta+}..O_2^{\delta-}) \rightarrow {}^1(M..O_2^*, {}^1\Delta_g)$. On the other hand, Schmidt's alternative kinetic model indicate that triplet ground state oxygen is formed via the internal conversion of $^3(^3M..O_2, {}^3\Sigma_g^-) \rightarrow {}^3(M..O_2, {}^3\Sigma_g^-)$ and/or mediated by the charge transfer complex, i.e., $^3(^3M..O_2, {}^3\Sigma_g^-) \rightarrow {}^3(M^{\delta+}..O_2^{\delta-}) \rightarrow {}^3(M..O_2, {}^3\Sigma_g^-)$. The energy gap relation for the dissociation of the encounter complexes $^{1,3}(^3M..O_2, {}^3\Sigma_g^-)$, leading finally to the formation of excited and ground states of molecular oxygen, has also been treated differently by Schmidt and co-workers. Recently [10,20], we have derived an energy gap relation (Eq. (14)) in an attempt to evaluate the rate constant in the absence of charge transfer assisted quenching, $k_{T\Delta}^{\Delta E}$ in cyclohexane. According to our treatment, at a particular excess energy there is a lower value for $k_{T\Delta}$ which is likely to have an energy gap dependence less steep than that given by Siebrand and Williams [66–68] for $T_1 \rightarrow S_0$ radiationless transitions in aromatic hydrocarbons, a curve has been drawn to fit through the points for compounds with high oxidation potential which give the lowest values for $k_{T\Delta}$ which can be interpreted as defining values equal to or at least close to the values of $k_{T\Delta}$ which pertain when charge transfer assisted energy transfer is neglected. Such a treatment is of course limited by the available data and might change slightly if lower values of $k_{T\Delta}$ are reported at a particular ΔE value.

Schmidt and co-workers [14,15,29] have found that for a series of sensitizers with strongly varying $E_T \leq 220\,kJ\,mol^{-1}$, the rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$ and $k_T^{3\Sigma}/3$ depend on the excess energy ΔE for the formation of $O_2^*(^1\Sigma_g^+)$, $O_2^*(^1\Delta_g)$ and $O_2(^3\Sigma_g^-)$ from $^{1,3}(^3M..O_2, {}^3\Sigma_g^-)$ encounter complexes in CCl_4. They have suggested that these rate constants for the non-charge transfer assisted quenching can be described by an empirical polynomial fit if the oxidation potentials $\geq 1.8\,V$ versus SCE. Based on their results which included the formation of $O_2^*(^1\Sigma_g^+)$ they assumed a fast and fully established ISC equilibrium for the encounter complexes, $^{1,3,5}(^3M..O_2, {}^3\Sigma_g^-)$, but only a comparatively slow ISC between charge transfer complexes, $^{1,3}(M^{\delta+}..O_2^{\delta-})$, and gave recently a three dimensional presentation that correlates these rate constants with ΔE and E_{ox}. {full details of the kinetic schemes and differences are given previously see for example Refs. [10,14,15,20,29]}.

3.2. Quenching of the excited singlet states

The situation of quenching of the excited singlet state by molecular oxygen is much more complex than in the case of excited triplet states quenching by molecular 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^S defined in Scheme 1 are rarely reported. Potashnik et al. [6] showed that f_T^S was unity in the case of eight aromatic hydrocarbons in toluene as solvent, but in the range 0.36–1.0 when acetonitrile is used. More recently, values of f_T^S less than unity have been reported for several aromatic hydrocarbons in acetonitrile by Sato et al. [7]. Wilkinson et al. [8,9] showed that for anthracene and several of its derivatives, f_T^S were found to be unity in cyclohexane and to vary from 0.6 to one in acetonitrile. Recently we have shown that f_T^S values are approaching unity for 11 aromatic hydrocarbons in cyclohexane [10] and varies from 0.50 to 1.0 in acetontrile [11] for the same set of compounds. Values of f_T^S 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 [7,9,11]. Values of f_Δ^S are also rarely reported in literature [1,2]. McLean et al. [12] measured the efficiencies of singlet oxygen production f_Δ^S from the excited singlet states of seven compounds in benzene solution and reported values of zero 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^S values of unity, as did Usui et al. [13] who reported f_Δ^S values for seven aromatic hydrocarbons in cyclohexane. The assumption of f_T^S values of unity may be justified in these two cases since the solvents used were non-polar. Wilkinson et al. [8,9] have reported the efficiencies of singlet oxygen production from the singlet and triplet states of a series of anthracene derivatives in cyclohexane [8] and acetonitrile [9], where the values of f_Δ^S measured in acetonitrile as a solvent are lower
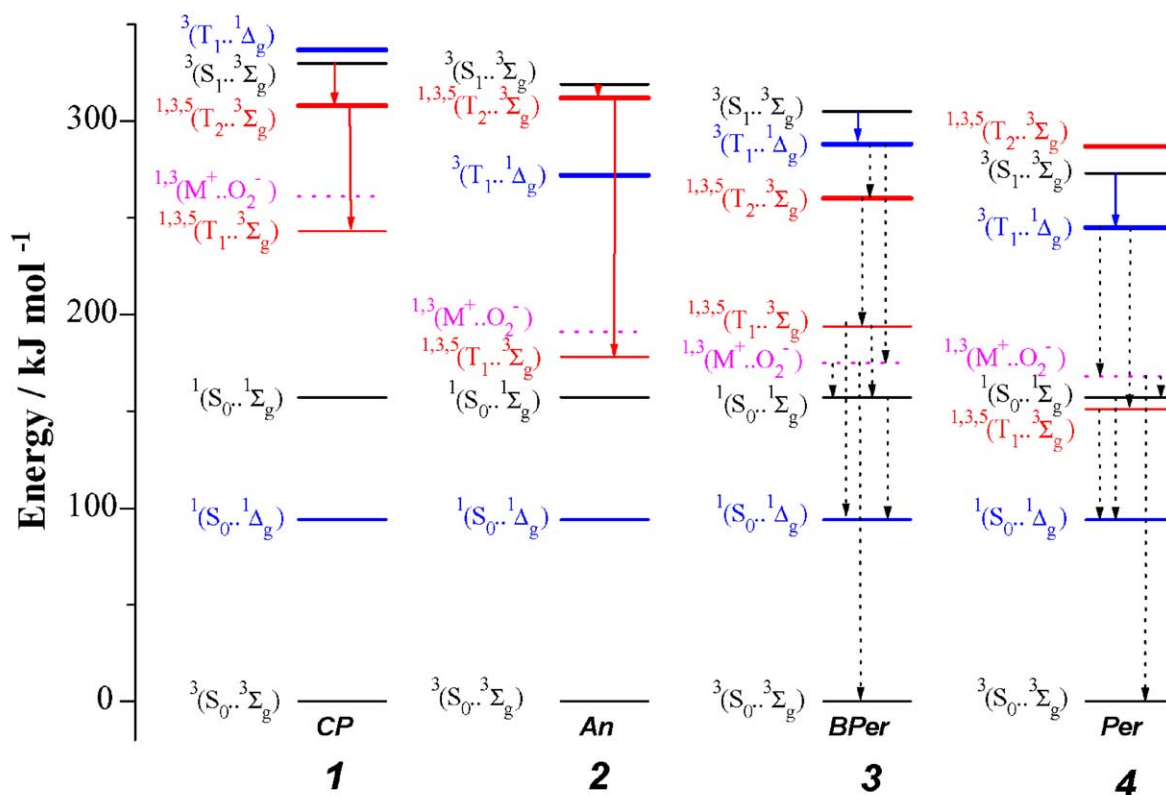
Fig. 3. Schematic electronic energy level diagram for encounter complexes (M..O_2) formed between aromatic hydrocarbons (M) and molecular oxygen in acetonitrile. Labels are CP, cyanophenanthrene; An, anthracene; BPer, benzoperylene; and Per, perylene.

than those reported in cyclohexane for the same compounds and vary from 0 to 0.50. Recently we have reported [10,11] the efficiencies of singlet oxygen production from the excited singlet states for 11 aromatic hydrocarbons in acetonitrile and cyclohexane. We have shown that [11] in acetonitrile f_Δ^S is zero for eight of the compounds and varies from 0.25 to 0.30 for the other four compounds in acetonitrile while in cyclohexane [10], perylene was the only compound shown to give f_Δ^S values of 0.28 and zero for the rest of compounds.

The efficiency of singlet oxygen production from the excited singlet state, f_Δ^S, is about 0.30 ± 0.05 for 1,2;5,6-dibenzanthracene, pyrene, fluoranthene, 1,11-benzoperylene and perylene and about zero for the rest of compounds. The energy levels of the encounter complexes between some of these compounds and oxygen are shown in Fig. 3. The arrangement of the energy levels of the encounter complexes of other molecule belongs to the arrangement of any of those shown in Fig. 3. In other words the arrangements shown in Fig. 3 represent the different possibilities for the set of compounds under investigation, for example the arrangement of the energy levels of 2,6-dimethoxynaphthalene and phenanthrene resembles that for cyanophenanthrene (set 1) while the arrangement of the energy levels of naphthalene, acenapthene and 1,2-benzanthracene resembles that for anthracene (set 2), whereas 1,2;5,6-dibenzanthracene, pyrene and fluoranthene resembles that of 1,11-benzoperylene (set 3) and case number (4) for perylene only. For these four cases:

1. For 2,6-dimethoxynaphthalene, phenanthrene and cyanophenanthrene, the condition that $\Delta E_{ST} \geq E(^1\Delta_g)$; 94 kJ mol^{-1} is not fulfilled. In other words, the energy of the encounter complex $^3(T_1..^1\Delta_g)$ is higher than that of $^3(S_1..^3\Sigma_g^-)$, therefore, singlet oxygen production is not possible in this case. For these three compounds $f_\Delta^S \approx 0$ (Table 1).

2. For naphthalene, acenapthene, 1,2-benzanthracene and anthracene, the internal conversion from the encounter complex $^3(S_1..^3\Sigma_g^-)$ and the efficiency of formation of the triplet encounter complex $^3(T_2..^3\Sigma_g^-)$ which can undergo internal conversion directly to give $^3(T_1..^3\Sigma_g^-)$ by-passing the $^3(T_1..^1\Delta_g)$ state which can then dissociate to give $^3M^*(T_1) + O_2(^3\Sigma_g^-)$ without energy transfer is the domination reaction pathway in this case. Thus very low values of f_Δ^S in this case can be attributed to the occurrence of these same processes, since the energies of the encounter complexes are in the order $(S_1..^3\Sigma_g^-) > (T_2..^3\Sigma_g^-) > (T_1..^1\Delta_g) > (T_1..^3\Sigma_g^-)$. The ordering of the energy levels of $(S_1..^3\Sigma_g^-) > (T_2..^3\Sigma_g^-) > (T_1..^3\Sigma_g^-)$ for phenanthrene and cycnophenanthrene (case 1) and for naphthalene, acenapthene, 1,2-benzanthracene and anthracene (case 2) as $(S_1..^3\Sigma_g^-) > (T_2..^3\Sigma_g^-) > (T_1..^1\Delta_g) > (T_1..^3\Sigma_g^-)$ explains the high values of f_T^S and k_{ST} in these two cases (Tables 1 and 2) with one exception for 2,6-
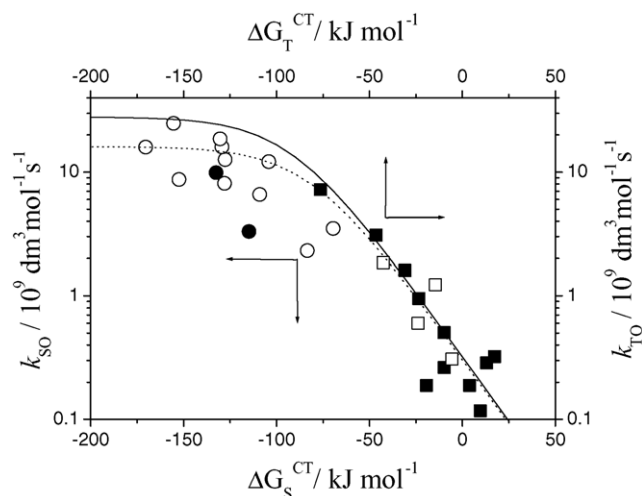
Fig. 4. Dependence of the net quenching rate constants k_{SO} ($\bigcirc$) and k_{TO} ($\blacksquare$), calculated using Eqs. (8) and (10), respectively, on the free energy changes ΔG_S^{CT} and ΔG_T^{CT}, and those taken from Ref. [11] for k_{SO} ($\bullet$) and k_{TO} ($\square$).

dimethoxynaphthalene where f_T^S values is 0.25. This low value of f_T^S in this case can be attributed to the competition with radical ion pair generation.

3. For 1,2;5,6-dibenzanthracene, pyrene, fluoranthene and 1,11-benzoperylene, the ordering of energy levels within the encounter complexes, $(S_1..^3\Sigma_g^-) > (T_1..^1\Delta_g) > (T_2..^3\Sigma_g^-) > (T_1..^3\Sigma_g^-)$, also explains why in these compounds singlet oxygen is produced. In addition, the values of $k_{S\Delta}$ are high enough (Table 2) to compete with the internal conversion to the $(T_2..^3\Sigma_g^-)$ complex state since this lies at a lower energy than $(T_1..^1\Delta_g)$ yielding f_Δ^S of about 0.3 for all of them.

4. For perylene the fact that the energy of the $(T_2..^3\Sigma_g^-)$ state lies above that of $(S_1..^3\Sigma_g^-)$ easily explains why f_Δ^S is not zero in this case. Other deactivation pathways that compete with the dissociation of $(T_1..^1\Delta_g)$ encounter complex and hence reduce the value of f_Δ^S are indicated by dashed arrows as shown in Fig. 3.

The fraction of the excited singlet state quenching by oxygen to give triplet state has been found to approach unity in non-polar solvents and very rare to be unity in polar solvents showing a slight dependence on E_{ox} for most of the compounds (see Table 1) which point to the importance of charge transfer interactions in this process. Combination of values of k_q^S and $1 - f_T^S$ as in Eq. (9) 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. Fig. 4 shows that the dependence of k_{SO} on ΔG_T^{CT} together with the data for the dependence of k_{TO} on ΔG_T^{CT}.

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 3 are included (dotted line in Fig. 4). However, the dependence of k_{TO}

on ΔG_T^{CT} can be fitted assuming that k_{TO} approach diffusion limit (solid line Fig. 4), where it can be seen that the solid line passes through the highest values of k_{SO} approaching k_d at high negative values of ΔG_S^{CT}. It is also 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 Fig. 4 is removed it is quite possible to draw a different curve through the experimental points which could yield a higher plateau rate constant i.e., approaching k_d at even more negative values of ΔG_S^{CT}.

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