

Quenching of electronically excited states by molecular oxygen in fluid solution

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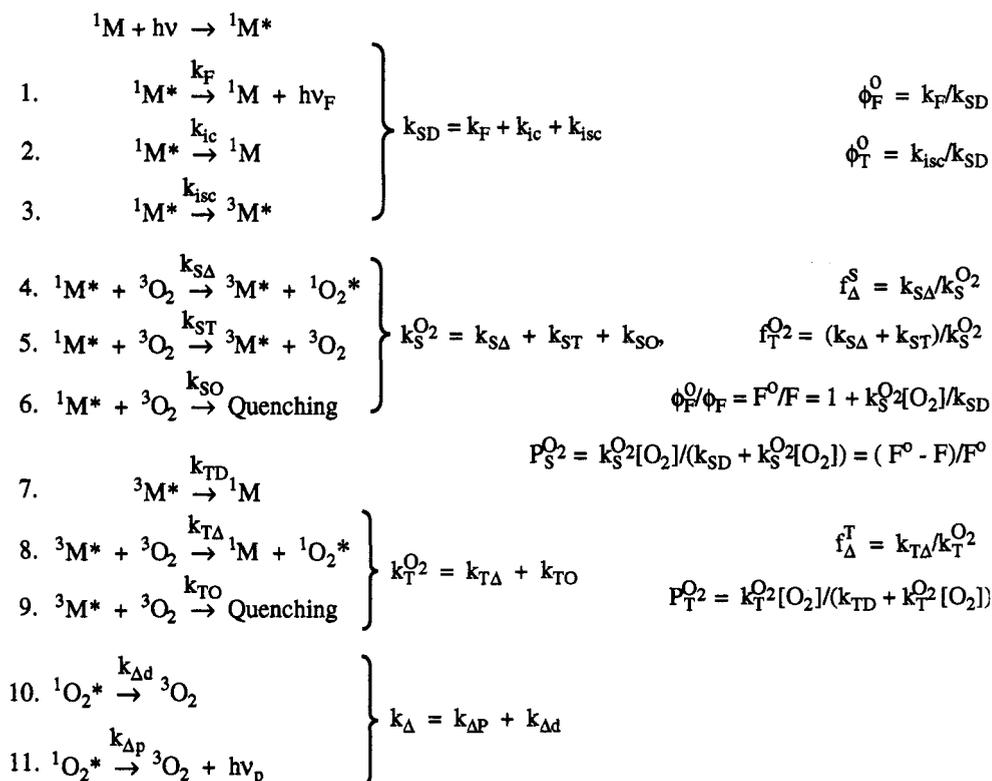
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Abstract: Rate constants, $k_T^{O_2}$, for quenching by oxygen of the triplet states of anthracene, biphenyl and naphthalene derivatives in acetonitrile and the efficiencies of formation thereby of singlet oxygen, f_Δ^T , are discussed in the light of the new values obtained for biphenyl derivatives. In the case of anthracene derivatives little variation in $k_T^{O_2}$ or f_Δ^T is observed but for biphenyl and naphthalene derivatives the rate constants $k_T^{O_2}$ decrease as their oxidation potential rises whilst f_Δ^T varies in the opposite direction. In the case of biphenyl derivatives f_Δ^T rises from 0.31 to 0.84 as $k_T^{O_2}$ decreases from 12.5 to $0.88 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ on going from 4,4'-dimethoxybiphenyl to 4-cyanobiphenyl. The mechanism of quenching via singlet and triplet channels is discussed and the importance of the energy of the charge transfer state involving electron transfer to oxygen, relative to the energy of the locally excited triplet state is established as important in determining $k_T^{O_2}$ and f_Δ^T . These results indicate that charge transfer assisted quenching occurs via both singlet and triplet complexes with only partial (up to 13.5%) charge transfer character.

INTRODUCTION

Quenching of excited states by molecular oxygen has been studied for decades [1-15]. Porter and Windsor [2] in 1958 reported a rate constant for quenching of triplet anthracene by oxygen in hexane solution of $4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ while Ware [3] in 1962 showed that fluorescence quenching by oxygen of the singlet state of anthracene occurred with rate constants ranging from 3 to $3.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in different solvents including p-xylene, benzene, methanol, n-heptane, toluene and acetone. In a set of classic studies Porter *et al* [4] showed that the rate constants for oxygen quenching of the triplet states of several aromatic hydrocarbons are less than those expected for a diffusion controlled reaction being $\leq 3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in benzene solution at room temperature which is about one ninth of the rate constants observed for oxygen quenching of excited singlet states of aromatic hydrocarbons [3]. However, the fractions of singlet and triplet states quenched by oxygen which produce singlet oxygen have more recently been shown to vary substantially from one compound to another [5-15]. The rate constant for quenching of triplet states by oxygen, $k_T^{O_2}$ and the fraction of triplet states quenched by oxygen which yield singlet oxygen f_Δ^T have been shown to depend on several factors including the triplet state energy, the nature of the excited state, the redox potential of the excited state and the polarity of the solvent. We have recently shown that for a series of substituted naphthalenes in acetonitrile, benzene and cyclohexane, the efficiency of singlet oxygen production during oxygen quenching of triplet states f_Δ^T increases while the value of $k_T^{O_2}$ decreases with increasing oxidation potential E_{OX}^M for naphthalene derivatives [9]. Furthermore the values of $k_T^{O_2}$ are higher and the values of f_Δ^T lower for naphthalene derivatives in more polar or polarisable solvents. This contrasts with the situation in the case of anthracene derivatives where $k_T^{O_2}$ values are close to one ninth of the diffusion controlled rate constant and show little variation with substituent or with the nature of the solvent except for the expected inverse dependence on viscosity [10]. We have also shown that for anthracene and several of its meso-derivatives in acetonitrile and cyclohexane, the efficiency of singlet oxygen production from triplet states quenched by oxygen f_Δ^T is in all cases unity within experimental error with the exception of 9-methoxyanthracene in acetonitrile where the value drops to one third [10]. In this work we extend our investigations of the mechanisms of quenching of triplet states by molecular oxygen to include a series of substituted biphenyls which have a wide range of half wave oxidation potentials.

Quenching of excited singlet states by oxygen may produce singlet oxygen when the gap between the first excited singlet and triplet states of the aromatic hydrocarbon is sufficient (94 kJ mol^{-1}) to produce singlet oxygen and can in addition catalyse further production of triplet states (see below). This has to be taken into account when interpreting the quantum yields of singlet oxygen production measured in any experiments where there is oxygen quenching of singlet states. The various competing reactions can be understood and the symbols used for the fundamentally important parameters are thereby defined by considering the nine steps shown in scheme 1.

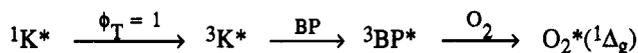
Scheme 1

Quenching of the lowest excited singlet state often leads to a Stern-Volmer relationship between F^O and F , the fluorescence intensities in the absence and presence of oxygen and oxygen concentration as given above. When the fraction of triplet states quench by oxygen is one i.e., $P_T^{O_2} = 1$ it follows that

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

Equation (1) relates the quantum yield of singlet oxygen production Φ_{Δ} to the extent of fluorescence quenching [5]. In order to determine f_{Δ}^S and f_{Δ}^T independent measurements are needed of ϕ_T^O and $f_T^{O_2}$, the triplet state formation efficiency in the absence of oxygen and as a result of oxygen quenching of the excited singlet state respectively.

Alternatively aromatic ketones can be used as sensitizers to populate the excited triplet states of the biphenyl derivatives by triplet energy transfer thus bypassing their excited singlet states and enabling f_{Δ}^T values to be determined without needing to consider oxygen quenching of their excited singlet states. This method has been employed successfully previously by ourselves [9,11], and by Gorman et al [12]. The biphenyl (BP) triplet state is thus populated with unit efficiency by energy transfer from an aromatic ketone (K), viz



If the triplet states of the sensitizers are formed with unit efficiency by energy transfer then Φ_{Δ} is simply given by

$$\phi_{\Delta} = f_{\Delta}^T P_T^{O_2} \quad (2)$$

We and others have established that energy transfer can occur with unit efficiency and this allows the easy determination of values of f_{Δ}^T by measuring Φ_{Δ} relative to a standard by comparing the amount of phosphorescence at 1270 nm from optically matched solutions subjected to Laser excitation.

Nanosecond flash photolysis and singlet oxygen yield measurements

Full experimental details have been given previously [8,13], and only a brief description is given here. For nanosecond flash photolysis studies and for the singlet oxygen yield measurements the 355nm harmonic of a Lumonics HY200 Q-switched Nd:YAG laser (8ns, 15mJ pulse⁻¹) was employed as the excitation source. Oxygen quenching rate constants were determined by sensitising the biphenyl triplet state with an aromatic ketone and measuring the rate of triplet decay in degassed and air-equilibrated solutions in which the oxygen concentration is 1.9×10^{-3} mol dm⁻³.

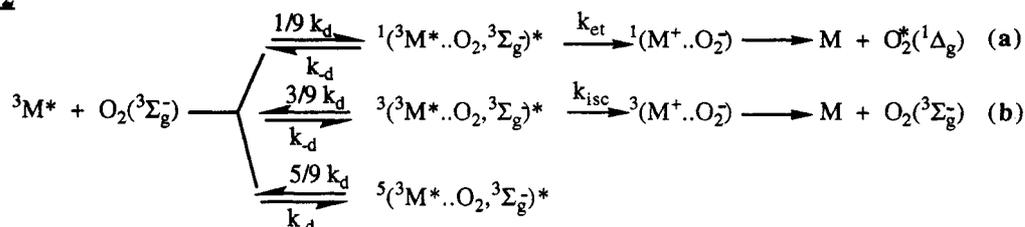
Singlet oxygen was detected by monitoring phosphorescence centred at 1270nm using a Judson germanium photodiode (J16-8SP-R05M, active diameter = 0.5cm) coupled to a Judson PA100 amplifier. The phosphorescence was detected at right angles to the exciting beam through a silicon cut-off filter. The laser energies employed did not exceed 0.7mJ pulse⁻¹. Individual luminescence traces were signal-averaged and fitted using a single exponential function to yield the luminescence intensity I_0 at $t=0$. The I_0 values were plotted against relative laser intensity to obtain plots which were linear below 0.5mJ pulse⁻¹. Comparison of the slopes of these plots yield relative singlet oxygen yields. Standards employed have included acridine, $\Phi_{\Delta}=0.82$ [14], phenalene, $\Phi_{\Delta}=0.95$ [15] and benzophenone/naphthalene in acetonitrile, $\Phi_{\Delta}=f_{\Delta}^T=0.62$ [5,9].

Previously [9] we have shown that energy transfer from benzophenone to biphenyl is almost certainly 100% efficient, by monitoring the triplet absorption of 1-methoxynaphthalene, at 440 nm, in degassed acetonitrile at low laser intensities (< 5 mJ pulse⁻¹) in the following optically matched solutions (a) benzophenone/ 0.1 mol dm⁻³ 1-methoxynaphthalene, and (b) benzophenone/ 0.1 mol dm⁻³ biphenyl / 10⁻³ mol dm⁻³ 1-methoxynaphthalene. For these two solutions, plots of the 1-methoxynaphthalene triplet absorbance at 440 nm versus laser intensity were constructed and found to have equal slopes to within experimental error (5%). Since introducing the biphenyl as an intermediate in the transfer of energy from triplet benzophenone to 1-methoxynaphthalene has no effect on the amount of triplet 1-methoxynaphthalene produced this strongly suggests that the efficiency of energy transfer from the ketone triplet to both biphenyl and to 1-methoxynaphthalene is 100%. In addition the triplet states of biphenyl and 4,4'-dimethoxybiphenyl have been populated in this work following energy transfer from two different aromatic ketones, namely benzophenone and 4-methoxy-acetophenone, the latter having a higher triplet state energy than benzophenone. The values of f_{Δ}^T obtained with the two different ketones as sensitizers were the same which is as expected if energy transfer from triplet ketones to biphenyls occurs with 100% efficiency.

RESULTS AND DISCUSSION

It is clear from figure 1 that an inverse correlation exists between f_{Δ}^T and $k_T^{O_2}$. This can be explained by considering Scheme 2 which expands steps 7 and 8 from Scheme 1 and includes spin statistical factors for physical quenching by oxygen.

Scheme 2



According to Scheme 2

$$k_T^{O_2} = (k_d/9)[k_{et}/(k_{et} + k_d)] + (3k_d/9)[k_{isc}/(k_{isc} + k_d)] \quad (3)$$

$$\text{and } f_{\Delta}^T = (k_d/9)[k_{et}/(k_{et} + k_d)]/k_T^{O_2} \quad (4)$$

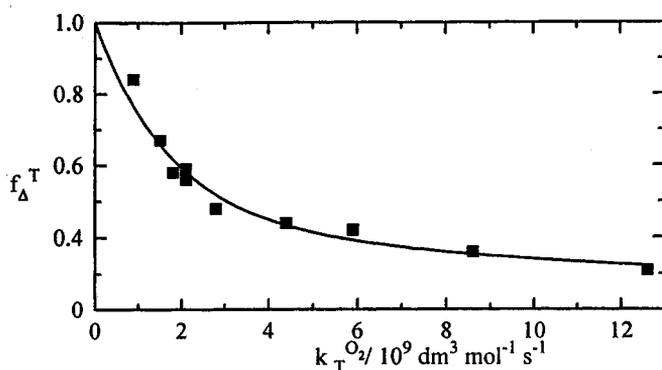


Figure 1 Dependence of f_{Δ}^T , the efficiency of formation of singlet oxygen resulting from oxygen quenching of the triplet states of biphenyl derivatives in acetonitrile on $k_T^{O_2}$, the rate constant for quenching by oxygen of these triplet states.

In the case of anthracene and several derivatives in acetonitrile we find that $k_T^{O_2}$ is approximately equal to $k_d/9$, in agreement with Gijzeman et al [4], implying exclusive quenching via the energy transfer channel to produce $O_2(^1\Delta_g)$ and f_{Δ}^T is one (cf equation (3) with $k_{et} \gg k_d$ and $k_{isc} \ll k_d$). This is interpreted as mainly being due to the spin statistical factor of one-ninth expected for oxygen quenching to give singlet oxygen indicating that only pathway (a) in Scheme 2 contributes efficiently to quenching. We have shown f_{Δ}^T is indeed one even in acetonitrile. However, much higher oxygen quenching rate constants have been reported in other studies [14-18]. The data presented in figure 1 where several values of $k_T^{O_2}$ exceed $k_d/9$ are similar to those we ourselves [9] have reported with $k_T^{O_2}$ in excess of $k_d/9$, for a series of naphthalene derivatives in acetonitrile, benzene and cyclohexane. For naphthalene and biphenyl derivatives in acetonitrile the maximum values observed for $k_T^{O_2}$ were 7.2 and $12.6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for 1-methoxynaphthalene and 4,4-dimethoxybiphenyl respectively.

In 1977, we first suggested [18] the involvement of charge transfer complexes in oxygen quenching in order to account for rate constants greater than $k_d/9$ and this mechanism has been used by many others to explain the mechanism of oxygen quenching of the triplet states of the aromatic molecules [7,19,20]. To interpret the results given in figure 1, it is interesting to calculate the limiting values according to Scheme 2. The efficiency of singlet oxygen generation from the triplet state would be 100% if only the quenching pathway (a) is involved and 25% if pathways (a) and (b) are both diffusion controlled. Thus if the oxygen quenching rate constant is $\leq k_d/9$ ($\sim 4.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), a limiting value of f_{Δ}^T equal to unity could occur, whereas a limiting value of 0.25 for f_{Δ}^T would be expected if the rate constant $= 4/9 k_d$ ($\sim 16.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) due to both channels being diffusion controlled if no intersystem crossing occurs between the singlet and triplet pathways. However, neither of these limiting values has been observed for the range of compounds studied here. For example in case of compounds with half-wave oxidation potentials $\geq 1.86 \text{ V}$ versus SCE, the quenching rate constants are less than $3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (i.e. $< 1/9 k_d$) and the observed f_{Δ}^T values lie in the range 0.49 - 0.85 which is far from unity. This behaviour could be attributed to enhanced intersystem crossing between the charge transfer states shown in Scheme 2 or to pathway (b) in scheme 2 being important even when $k_T^{O_2}$ is $< 1/9 k_d$.

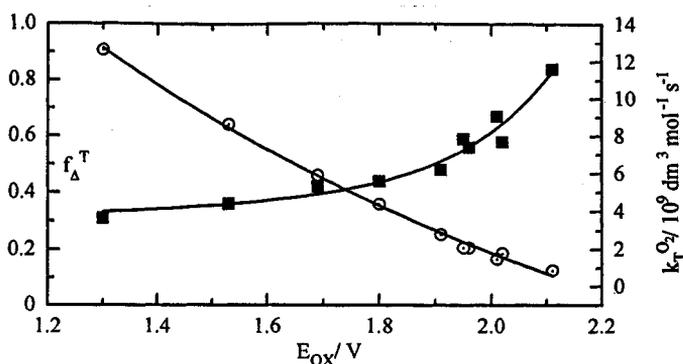


Figure 2 Dependence of f_{Δ}^T and $k_T^{O_2}$ on the half wave oxidation potential (E_{OX} vs SCE) of biphenyl derivatives in acetonitrile.

Varying the electron donating nature of the substituent on the biphenyl ring influences E_M^{OX} and the smooth dependence of $k_T^{O_2}$ and f_Δ^T on E_M^{OX} shown in figure 2 demonstrates the importance of charge transfer interactions. A good estimate for the free energy change (ΔG^{CT}) to form ion pairs from neutral molecules in acetonitrile as shown by Rehm and Weiler [21] is given by

$$\Delta G^{CT} = F[E_M^{OX} - E_{O_2}^{red}] - E_T + C \quad (5)$$

where F is the Faraday constant and $E_{O_2}^{red}$ is the half-wave reduction potential for O₂ ($^3\Sigma_g^-$) taken to be -0.78 V versus SCE [22]. C is the electrostatic interaction energy which is inversely proportional to the static relative permittivity, ϵ , of the solvent and since for acetonitrile $\epsilon = 37$ the term C is likely to be negligible in this case. A plot of the dependence of f_Δ^T and $k_T^{O_2}$ on ΔG^{CT} is very similar to the plot shown in figure 2. For compounds with a high value of E_M^{OX} and hence where ΔG^{CT} is positive $f_\Delta^T = 0.85$, i.e., f_Δ^T approaches the highest expected value of unity. This value may become less than unity due to state mixing imparting substantial CT character into the low lying excited states of M..O₂ complexes even when $E_{CT} > E_T$ i.e., when ΔG^{CT} is positive. When ΔG^{CT} is negative, f_Δ^T drops to 0.31 in the case of 4,4-dimethoxybiphenyl. Despite the large negative value of ΔG^{CT} , no radical formation was detected under our experimental conditions.

According to Scheme 2 the net rate constants for oxygen quenching k_q^1 and k_q^3 and the probabilities of quenching p_1 and p_3 via the singlet and triplet pathways, (a) and (b) respectively are given by

$$k_q^1 = f_\Delta^T k_T^{O_2} \quad (6)$$

$$p_1 = 9k_q^1/k_d = k_{et}/(k_{et} + k_d) \quad (7)$$

$$k_q^3 = (1 - f_\Delta^T) k_T^{O_2} \quad (8)$$

$$p_3 = 3k_q^3/k_d = k_{isc}/(k_{isc} + k_d) \quad (9)$$

$$p_1/(1 - p_1) = k_{et}/k_d \quad (10)$$

and
$$p_3/(1 - p_3) = k_{isc}/k_d \quad (11)$$

Taking the diffusion controlled rate constant for oxygen quenching in acetonitrile as $3.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [23] and plotting $\ln\{p_1/(1-p_1)\}$ and $\ln\{p_3/(1-p_3)\}$ against ΔG^{CT} gives two parallel linear plots of slope equal to $-0.024 \text{ mol kJ}^{-1}$ in contrast to a slope of $-0.178 \text{ mol kJ}^{-1}$ expected for quenching involving complete electron transfer. This implies quenching is via a charge transfer complex with only 13.5% charge transfer character i.e., oxygen quenching occurs by an exciplex mechanism similar to that recently proposed by Kuzmin [24] and there is a linear free energy relationship between the free energy of activation for oxygen quenching via both singlet and triplet pathways and ΔG^{CT} . Unfortunately it is not possible on the basis of this data to prove the presence or absence of intersystem crossings between the singlet and triplet M..O₂ charge-transfer complexes shown in scheme 2.

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