

Factors which determine the efficiency of sensitized singlet oxygen production

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Abstract. Nanosecond laser photolysis measurements of sensitized phosphorescence from oxygen have been used to obtain values for singlet oxygen formation efficiencies during oxygen quenching of excited singlet and triplet states of anthracene and naphthalene derivatives. Oxygen quenching of excited singlet states of anthracene and dicyanoanthracene in cyclohexane has been shown to lead to catalysed production of triplet states with unit efficiency in both cases, but concurrent production of singlet oxygen only occurs in the case of 9,10-dicyanoanthracene with efficiency close to unity whereas the efficiency for singlet oxygen production due to direct oxygen quenching of excited singlet anthracene is close to zero. In contrast to these results, oxygen quenching of the triplet states of anthracene and dicyanoanthracene in cyclohexane yields singlet oxygen with unit efficiency whereas the singlet oxygen formation efficiency during oxygen quenching of triplet 1-ethylnaphthalene is only 0.86 in cyclohexane and drops to 0.51 in acetonitrile. This solvent dependence demonstrates the role which charge transfer interactions play in determining singlet oxygen yields. Further information concerning the decay of excited oxygen–aromatic hydrocarbon charge-transfer complexes have been obtained from picosecond laser pump-probe studies where direct excitation is into the charge-transfer bands of oxygenated 1-ethylnaphthalene. Following the excitation of the charge-transfer complex, the triplet state of 1-ethylnaphthalene is rapidly produced with an efficiency which shows a marked solvent dependency, being 0.4 and 0.8 in acetonitrile and cyclohexane, respectively. The measured yields of singlet oxygen formation following excitation into 1-ethylnaphthalene-oxygen charge-transfer complexes are 0.36 and 0.78 in these two solvents which is greater than that expected on the basis of the measured triplet yields. Mechanisms of quenching of excited states by oxygen which explain these results are discussed.

Keywords. Singlet oxygen yields; oxygen quenching; charge transfer absorption.

1. Introduction

It is well known that molecular oxygen is a paramagnetic molecule which is ubiquitous and efficiently quenches electronically excited states in dilute fluid solution (Birks 1970). The ground electronic state of molecular oxygen has zero angular momentum about its internuclear axis, contains two unpaired p -electrons and is given the group theoretical symbol ${}^3\Sigma_g^-$. The two electronically excited states of oxygen which arise from the same electron configuration, both with spin pairing of these two electrons, are the ${}^1\Delta_g$ and the ${}^1\Sigma_g^+$ states which lie 94 and 157 kJ mol⁻¹ respectively above the ground state. Oxygen is one of the most efficient quenchers of electronically excited

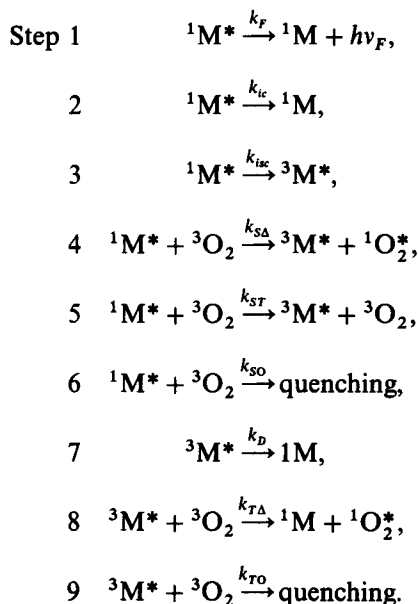
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states and it is often assumed that electronic excitation energy is transferred to oxygen with high efficiency when spin statistical factors are taken into account. In a set of classic studies, Gijzeman *et al* (1973) showed that the rate constants 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 (Ware 1962). 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. (Redmond and Braslavsky 1988a; Saltiel and Atwater 1988; McLean *et al* 1990; Wilkinson *et al* 1993). 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 exceeds 94 kJ mol^{-1} 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 by considering the nine steps shown below from which it follows that

$$\phi_F^0 = \frac{k_F}{k_F + k_{ic} + k_{isc}} \quad \text{and} \quad \phi_T^0 = \frac{k_{isc}}{k_F + k_{ic} + k_{isc}}, \quad (1)$$

where ϕ_F^0 and ϕ_T^0 are the quantum yields of fluorescence and of triplet state production in the absence of oxygen, respectively.



We can define the fraction of singlet states quenched by oxygen as

$$P_S^{\text{O}_2} = k_{\text{O}_2}^S [\text{O}_2] / (k_D^S + k_{\text{O}_2}^S [\text{O}_2]), \quad (2)$$

where

$$k_{O_2}^S = k_{S\Delta} + k_{ST} + k_{SO} \text{ and } k_D^S = k_F + k_{ic} + k_{isc}.$$

The quantum yield of triplet production in the presence of oxygen $\phi_T^{O_2}$ is given by

$$\phi_T^{O_2} = \phi_T^0(1 - P_S^{O_2}) + f_T^{O_2} P_S^{O_2}, \quad (3)$$

where $f_T^{O_2}$ is the fraction of singlet states quenched by O_2 which yield triplet states. Note that step 6 represents quenching of the singlet state by oxygen by any mechanism which does not produce either singlet oxygen or triplet states i.e., other than those shown in steps 4 and 5. The quantum yield of singlet oxygen production by sensitization ϕ_Δ is given by the sum of the contributions due to oxygen quenching of singlet and triplet states i.e.

$$\phi_\Delta = \phi_\Delta(S_1) + \phi_\Delta(T_1). \quad (4)$$

If f_Δ^S and f_Δ^T are defined as the fractions of S_1 and T_1 states respectively quenched by oxygen which give $O_2^*(^1\Delta_g)$ it follows that

$$\phi_\Delta = f_\Delta^S P_S^{O_2} + \phi_T^{O_2} f_\Delta^T P_T^{O_2}, \quad (5)$$

where $P_T^{O_2}$ equals that fraction of the triplet states which are quenched by oxygen, which is often close to unity because of the long lifetimes of many triplet states.

Quenching of the excited singlet state leads to a Stern–Volmer relationship between the fluorescence quantum yields in the absence and presence of oxygen as given by (6) where F^0 and F represent the fluorescent intensity of the sensitizer in the absence and presence of oxygen i.e.

$$\phi_F^0/\phi_F = F^0/F = 1 + k_{O_2}^S [O_2]/k_D^S. \quad (6)$$

When $P_T^{O_2} = 1$, combining (2), (3), (5) and (6) gives

$$\phi_\Delta(F^0/F) = (f_\Delta^S + f_T^{O_2} f_\Delta^T) [(F^0/F) - 1] + \phi_T^0 f_\Delta^T, \quad (7)$$

which can be used to obtain information concerning the crucial factors; however, one needs independent measurements of ϕ_T^0 and $f_T^{O_2}$ to determine f_Δ^S and f_Δ^T .

Alternatively one can produce the triplet states of the sensitizer with unit efficiency by energy transfer using aromatic ketones as triplet energy donors. Then (5) becomes

$$\phi_\Delta = f_\Delta^T P_T^{O_2}. \quad (8)$$

This allows values of f_Δ^T to be determined. We have recently employed this method used previously by ourselves (Garner and Wilkinson 1976) and others (Gorman *et al* 1987) to demonstrate the dependence of f_Δ^T for a series of naphthalene derivatives in benzene on the oxidation potential of the sensitizer (McGarvey *et al* 1992).

The perturbing effects of dissolved oxygen on the UV/Vis absorption spectra of organic molecules is a well-known phenomenon which was first studied in detail by Evans (1957) and subsequently discussed by Tsubomura and Mulliken (1960) and Birks (1970). The additional absorption bands observed include the lowest energy transition which corresponds to the $S_0 \rightarrow T_1$ transition of the organic molecules in intimate contact with an oxygen molecule. More intense absorption observed at

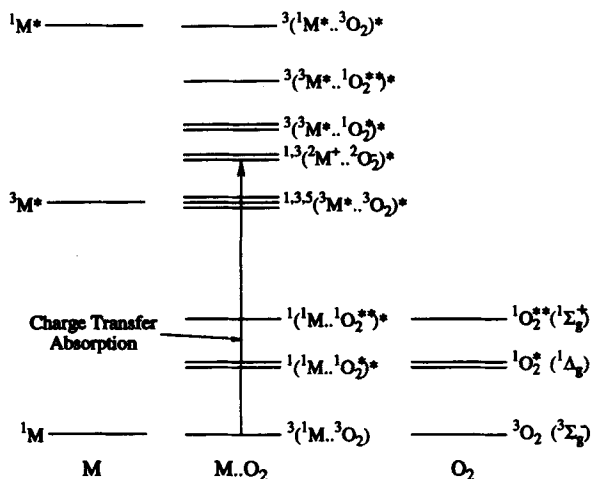


Figure 1. Schematic diagram of the lower energy levels of the $M..O_2$ complex between an aromatic molecule, M , and molecular oxygen, O_2 .

shorter wavelengths is often attributed to CT transitions within ${}^3(M..O_2)$ contact complexes (see figure 1) and this assignment is supported by the broad structureless appearance of the bands. In this paper, we exploit the optical absorption properties of oxygen/organic molecule contact complexes to directly populate, using both nanosecond and picosecond laser pulses, excited state complexes which may be involved in the dynamic quenching of excited states by oxygen.

2. Experimental

2.1 Materials

Anthracene (Aldrich Gold Label), naphthalene (Aldrich, scintillation grade, > 99%), 1-ethylnaphthalene (Fluka, 99%), benzophenone (BP) (Aldrich Gold Label) and *p*-methoxyacetophenone (PMAP) (Aldrich, 99%) were used as received. Acridine (Aldrich) was recrystallised from ethanol and 9,10-dicyanoanthracene (Kodak) was recrystallised from benzene. Acetonitrile (Aldrich, spectrophotometric grade) was dried by refluxing over calcium hydride. All other solvents were spectrophotometric grade from Aldrich and were used as received.

2.2 Picosecond pump-probe measurements

Solutions of 1.5 M 1-ethylnaphthalene (EN) in cyclohexane and acetonitrile were equilibrated with 2–4 atmospheres of oxygen yielding absorbances of ~ 0.3 around 355 nm compared with ~ 0.05 for air-equilibrated solutions. The absorbance due to the EN/O_2 contact complex exhibits a linear dependence on oxygen concentration under our conditions. The picosecond time-resolved absorption measurements were carried out at the Rutherford-Appleton Laboratory Laser Support Facility. The picosecond laser system was a frequency-doubled mode-locked Nd/YAG pumping a dye laser operating at 706 nm. The pump and probe wavelengths were obtained by

frequency-doubling to give 353 nm and mixing of 1064 nm and 706 nm to give 424 nm. The operating conditions were as follows: pump wavelength = 353 nm, pump energy = 4 μ J; probe wavelengths = 424 nm and 706 nm, pulse duration = \sim 5 ps, irradiation area = 0.8 mm². The probe wavelengths are suitable for detection of the EN triplet state (424 nm) and the EN radical cation (706 nm). We are not aware of a documented spectrum for EN⁺ but expect that it will have a similar spectrum to the naphthalene radical cation which is well documented (Liu *et al* 1992). The yield of EN triplet state following CT excitation was measured by comparison of the triplet state absorption, observed at 424 nm, 400 ps after excitation with that from an identical optically-matched air-equilibrated solution containing BP or PMAP. Under our conditions ([EN] = 1.5 M) energy transfer is complete within 300 ps. Both ketones give the same yield of sensitised ³EN* demonstrating that energy transfer from the triplet state of these aromatic ketones proceeds with 100% efficiency giving an effective EN triplet state yield of unity for these solutions.

2.3 Nanosecond flash photolysis and singlet oxygen yield measurements

For nanosecond flash photolysis studies and for the singlet oxygen yield measurements the 355 nm harmonic of a Lumonics HY200 Q-switched Nd/YAG laser (8 ns, 15 mJ pulse⁻¹) was employed as the excitation source. Oxygen-quenching rate constants were determined by sensitising the EN triplet state with an aromatic ketone and measuring the rate of triplet decay in an air-equilibrated solution. Singlet oxygen was detected by monitoring the 0,0 vibronic band of the phosphorescence centred at 1270 nm (9) using a Judson germanium photodiode (J16-8SP-R05M, active diameter = 0.5 cm) 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 0.7 mJ 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 0.5 mJ pulse⁻¹. Comparison of the slopes of these plots yielded relative singlet oxygen yields. The fluorescence measurements with anthracene and dicyanoanthracene were carried out using a Perkin-Elmer 3000 fluorimeter and the oxygen concentrations were in the range 2.4–34.6–10⁻³ mol dm⁻³.

3. Results and discussion

The singlet-triplet energy gap in the case of many aromatic hydrocarbons, e.g. anthracene, naphthalene and their derivatives, is such that it is energetically possible to produce singlet oxygen via oxygen quenching of both excited singlet and triplet states i.e. by reactions (4) and (8) given earlier. According to (7) plots of $\Phi_{\Delta}(F^0/F)$ versus $[(F^0/F) - 1]$ should be linear and figure 2 shows that this applies to the data we obtained for anthracene and dicyanoanthracene in cyclohexane. The slopes and intercepts for these two compounds show very large differences. The slopes of these plots give values for $(f_{\Delta}^S + f_{\Delta}^T f_{\text{O}_2}^0)$ of 0.91 ± 0.05 and 1.95 ± 0.05 respectively for

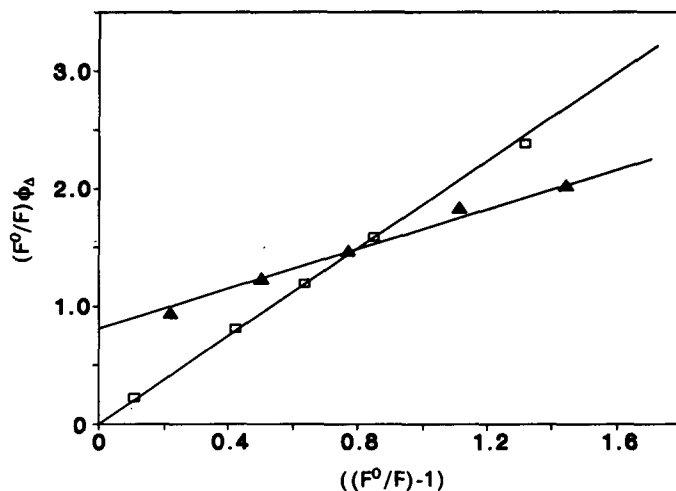


Figure 2. Plots according to (7) (see text) which illustrate the dependence of ϕ_{Δ} , the singlet oxygen yield, on the extent of fluorescence quenching by oxygen, where F^0 and F represent the fluorescence intensities in the absence and presence of oxygen, for (\blacktriangle) anthracene and (\square) dicyanoanthracene in cyclohexane.

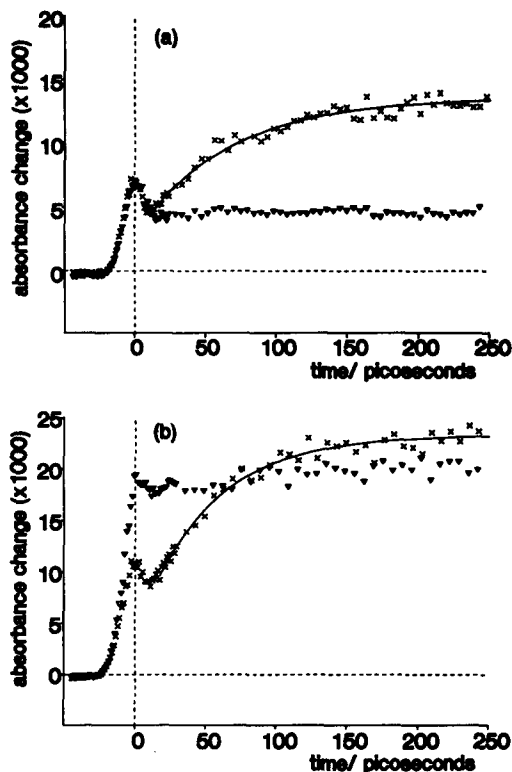


Figure 3. Picosecond absorption profiles observed for 1.5 mol dm^{-3} of 1-ethylnaphthalene in (a) acetonitrile and (b) cyclohexane; (∇) oxygenated with 3–4 atmospheres of oxygen, (\times) air-equilibrated containing benzophenone. The oxygenated and ketone-containing solutions were optically matched at the excitation wavelength (353 nm).

anthracene and dicyanoanthracene. The value for dicyanoanthracene is close to the maximum value of 2 which arises when $f_{\Delta}^S = f_{\Delta}^T = f_T^{O_2} = 1$ i.e. all these fractions are unity which applies when oxygen quenching is exclusively via steps 4 and 8. This is the situation for dicyanoanthracene in this solvent. Note that the intercept of the plot for dicyanoanthracene in figure 3 is 0 ± 0.05 which is consistent with $\Phi_T \approx 0$. In the case of anthracene, however, the intercept is equal to 0.77 ± 0.05 which equals $(f_{\Delta}^T \Phi_T^0)$ and since the triplet yield is reported to be 0.72 ± 0.05 (Horrocks and Wilkinson 1968) these values are consistent with $f_{\Delta}^T = 1.0 \pm 0.05$. Potashnik *et al* (1971) have shown that oxygen quenching of singlet anthracene does lead to enhanced triplet absorption with $f_T^{O_2} = 0.9 \pm 0.1$ in toluene and acetonitrile. It follows that f_{Δ}^S is close to zero for anthracene. The reason why f_{Δ}^S values is so different for anthracene and dicyanoanthracene is likely to be due to the same reason which causes the intersystem crossing yields of these two compounds to be so different, namely the presence or absence of an intermediate triplet state between the S_1 and T_1 states in these anthracene derivatives.

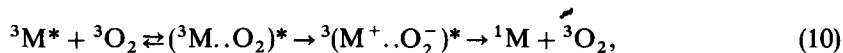
The probabilities of dissociation of collisional complexes of the type shown in figure 1 relative to the probability of internal conversion leading to energy dissipation in these complexes determines the values of f_{Δ}^S and f_{Δ}^T . In an attempt to understand such processes we have examined the singlet oxygen yields when excitation, under an elevated pressure of oxygen, was directly into the CT state (see figure 1) in comparison with the singlet oxygen yields observed via triplet sensitisation from triplet BP (or PMAP) in air-equilibrated 1.5 M EN solutions using optically matched solutions. The singlet oxygen yields from the sensitised samples were assumed to be the same as those measured by us using smaller EN concentrations (~ 0.05 M). In these measurements the standards used were acridine in acetonitrile, $\Phi_{\Delta} = 0.82$ (Redmond and Braslavsky 1988b) and *p*-methoxyacetophenone/0.1 M naphthalene in cyclohexane, $\Phi_{\Delta} = 0.92$ (Gorman *et al* 1991). Thus values of the singlet oxygen yields resulting from absorption to CT states of O_2 /EN complexes, Φ_{Δ}^{CT} , equal to 0.36 and 0.78 were obtained in acetonitrile and cyclohexane respectively.

Using 353 nm picosecond excitation of the same solutions, a 'prompt' increase in absorption at 424 nm where triplet naphthalene absorbs was observed (figure 3), which does not significantly decay over the timescales investigated (~ 1 ns). Thus the EN triplet state is produced within a few picoseconds i.e. within the risetime of our picosecond apparatus. Superimposed upon the rise in triplet state absorption we observe a rapid symmetrical rise and fall in absorption which follows the excitation pulse. This component is present regardless of whether the solution is oxygenated or not and so is not derived from the CT state. Also this rapid component is not observed with neat acetonitrile or cyclohexane but is observed in the case of neat benzene. This feature has been observed previously (Masuhara *et al* 1981; Miyasaka *et al* 1985) in studies of multiphoton absorption by neat aromatic liquids as a rapid component absorbing around 420 nm and was attributed to electron-aromatic ion production and geminate recombination. We believe a similar process is operating when 1.5 M EN solutions are subjected to 353 nm picosecond excitation. The consequence of this multiphoton absorption is the appearance of a relatively small long-lived (> 1 ns) absorption which may be due to the excited singlet or triplet state of EN or it may be due to the EN radical cation or a combination of these. Since we do not have the facility of spectral resolution with our picosecond measurements we are presently unable to identify this weak background absorption.

Using the picosecond apparatus and probing at 706 nm for the EN radical cation we observed only very small 'prompt' absorptions ($\sim 10^{-3}$) which were not sensitive to the concentration of oxygen. This agrees with our nanosecond photolysis measurements where we also were unable to detect significant absorption in the 680–720 nm region following excitation into the CT band using either solvent. However these observations contrast with the report by Kristiansen *et al* (1991) who detected the 1-methylnaphthalene radical cation in acetonitrile following CT excitation. Unfortunately no details concerning the amounts of radical cation so produced were given. Thus it is difficult to compare results.

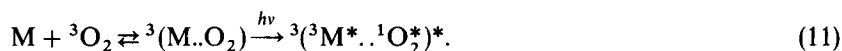
The varying efficiencies of triplet state formation (ϕ_T^{CT}) as a function of solvent is apparent from the traces shown in figure 3. The triplet yield determinations derived exclusively from the picosecond pump-probe measurements of optically matched solutions are 0.40 and 0.80 in acetonitrile and cyclohexane respectively. We have determined f_{Δ}^T for EN in acetonitrile and cyclohexane using triplet ketones as triplet energy donors and the values we obtained were 0.51 and 0.86 respectively. The value of the product $f_{\Delta}^T \phi_T^{CT}$ that is equal to the amount of singlet oxygen production, which would be expected following excitation to the charge transfer state on the basis of the observed yield of triplet state production, equals 0.20 and 0.69 in acetonitrile and cyclohexane respectively, which is not equal to our measured values of Φ_{Δ}^{CT} particularly in acetonitrile. Thus more singlet oxygen is produced from the charge transfer state than can be accounted for from the amount of triplet state produced. Another interesting feature of the data is the large solvent dependence of ϕ_T^{CT} . Thus in cyclohexane the triplet state production from the charge transfer state is very efficient ($\sim 80\%$) but in acetonitrile it is dramatically reduced to only 40%. This difference is clearly shown in figure 3.

In a previous paper (McGarvey *et al* 1992) we used the Rehm–Weller equation (Rehm and Weller 1970), neglecting the coulombic term, and calculated the free energy of the relaxed charge transfer states, ${}^1,3(M^+ \cdot O_2^-)^*$ to be $\sim 30 \text{ kJ mol}^{-1}$ below the localised triplet for EN. In acetonitrile where any coulombic correction will be small since it has a dielectric constant of 37.5 the excited complexes ${}^1,3(M^+ \cdot O_2^-)^*$ are very likely to lie below the localised triplet and to be populated followed the formation of ${}^3M^*$ by energy transfer or following triplet state production following charge transfer absorption. There is a large difference between the f_{Δ}^T and k_q^T values for EN in the two solvents. In cyclohexane the values of f_{Δ}^T and k_q^T are 0.86 and $1.6 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ respectively, while for acetonitrile the values are 0.51 and $3.3 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. These numbers indicate that (9) is more important in acetonitrile than in cyclohexane due to the more favourable CT interactions in the more polar solvent. It is likely that this is due to the catalysed intersystem crossing via the triplet channel i.e.



which does not produce singlet oxygen. In cyclohexane which has a dielectric constant of 2.02 it is quite likely that the relaxed charge transfer states, ${}^1,3(M^+ \cdot O_2^-)^*$ lie above the localised triplet and in the absence of CT-mediated quenching the triplet channel is impeded relative to the singlet channel because of poor Franck–Condon factors (Gijzeman *et al* 1973). Thus we would expect that deactivation of the initially prepared excited state complex to give ground state products would be faster in acetonitrile than in cyclohexane. This means that separation of $({}^3M \cdot O_2)^*$ to yield the triplet state would be more important in cyclohexane as observed.

Since the triplet energies of naphthalene and 1-methylnaphthalene are 255 and 249 kJ mol⁻¹ respectively (Murov 1973) it is likely that the energy of ³(³M*..¹O₂*)* i.e., the complex formed by association of the triplet state of EN and singlet oxygen, will be ~ 343 kJ mol⁻¹, which is slightly higher than the excitation energy used in these experiments (338 kJ mol⁻¹). In fact, Dijkgraaf and Hoijtink (1963) have reported a broad shoulder around 350 nm in oxygenated naphthalene solutions which they attribute to the simultaneous transition described by



Thus the simplest explanation for the fact that Φ_{CT}^A is higher than $f_{\Delta}^T \Phi_{CT}^{CT}$ is that excitation at 353 and 355 nm gives both ³M* and singlet oxygen following dissociation of ³(³M*..¹O₂*)* formed either as a result of direct absorption to this doubly excited complex or following internal conversion from the initially formed Franck–Condon charge transfer complex ³(M⁺..O₂⁻)_{FC}*. In the case of acetonitrile and cyclohexane, respectively, this would require a quantum yield of 0.16 and 0.08 for this process in these two solvents. The fact that several organic compounds, which have energy gaps between their lowest singlet and triplet states greater than 94 kJ mol⁻¹ give singlet oxygen yields greater than one (Tsubomura and Mulliken 1960; Saltiel and Atwater 1988; Kanner and Foote 1992) when excited into their lowest singlet excited states, demonstrates that this doubly excited state dissociates to give both the triplet state and singlet oxygen when it is populated in the case of many other compounds.

4. Conclusions

We have shown how fluorescence quenching measurements combined with singlet oxygen yield measurements can be used to obtain values of f_{Δ}^S and f_{Δ}^T , the fractions of singlet oxygen formed for oxygen quenching of excited singlet and excited triplet states, respectively. The values of f_{Δ}^S for anthracene and 9,10-dicyanoanthracene are 0 and 0.95 ± 0.05 respectively. Unfortunately there are very few f_{Δ}^S values in the literature (see Saltiel and Atwater 1988 and Wilkinson *et al* 1993 and references therein). Thus it is difficult at present to speculate on the reasons for observed variations in f_{Δ}^S . By contrast, many authors have obtained values for f_{Δ}^T , and recent measurements by ourselves (McGarvey *et al* 1992) have indicated the important role charge transfer interactions play in increasing the probability of quenching by pathways which do not lead to energy transfer. We have used picosecond pump probe techniques following exclusive direct excitation of charge transfer complexes of 1-ethylnaphthalene/O₂ to probe the fate of excited charge transfer complexes. We observe a prompt production of the triplet state is less than 5 picoseconds. We have shown that the quantum yields of prompt triplet states produced are 0.4 and 0.8 in acetonitrile and cyclohexane, respectively, i.e. we have shown that the value is strongly dependent on the polarity of the solvent. The quantum yield of singlet oxygen production following charge transfer excitation is also solvent dependent; however, the values obtained for Φ_{Δ}^{CT} are 0.36 and 0.78 which are greater than one would expect on the basis of the measured triplet yields. We suggest that the excited charge transfer complex can dissociate to give both triplet states and singlet oxygen immediately following excitation.

Acknowledgements

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