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Mechanism of Quenching of Triplet States by Molecular Oxygen: Biphenyl Derivatives in Different Solvents

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The bimolecular rate constants $k_T^{O_2}$ for oxygen ($O_2(^3\Sigma_g^-)$) quenching and the efficiencies $f_\Delta{}^T$ with which singlet oxygen ($O_2{}^*(^1\Delta_g)$) is thereby produced are reported for a range of substituted biphenyl triplet states in acetonitrile, benzene, and cyclohexane. The magnitudes of $k_T^{O_2}$ and $f_\Delta{}^T$ are inversely correlated, and both parameters exhibit pronounced sensitivity to the oxidation potential (E_M^{OX}) of the biphenyl derivative and to the solvent polarity. It has been observed that the quenching rate constant increases as the oxidation potential of the biphenyl derivative decreases and increases as the solvent polarity increases whereas the efficiency of singlet oxygen production increases with the oxidation potential and decreases with increasing solvent polarity. When solvent viscosity changes are allowed for by calculating the diffusion controlled rate constant, k_d, it is established that $k_T^{O_2}/k_d$ values are comparable when the electrostatic interaction energy of charge transfer complexes are taken as 0, 3, and 20 kJ mol^{-1} for acetonitrile, benzene, and cyclohexane, respectively. An improved charge transfer mediated mechanism of quenching based on singlet and triplet channels for oxygen quenching is invoked to discuss these results with the triplet channel only operating when charge transfer is favorable. However, to get a good fit to the data, it is necessary to introduce direct formation of singlet oxygen production from the singlet encounter complexes in competition with charge transfer assisted singlet oxygen production. The free energy of activation for charge transfer assisted quenching by oxygen via singlet and triplet channels is shown to have a linear dependence on the free energy change for full charge transfer, but the indications are that quenching is via singlet and triplet charge transfer complexes with only partial charge transfer character being 12.5%, 14.5%, and 17% in acetonitrile, benzene, and cyclohexane, respectively. An explanation is offered as to why the less polar solvents show the larger fractional charge transfer in the transition states involved in the quenching mechanism.

Introduction

It is well-known that singlet oxygen is produced with varying efficiency as a consequence of quenching of both excited singlet and triplet states. Despite the intense research carried out over the last three decades on the mechanisms of quenching of electronically excited states by molecular oxygen, several aspects remain unclear.[1−13] In a recent compilation[1] of the quantum yields for the photosensitized formation of the lowest electronically excited state of molecular oxygen in solution, we reported the quantum yields of singlet oxygen production, Φ_Δ, of 755 different compounds in a wide range of solvents. Despite all these data the reasons why certain compounds yield singlet oxygen with high and others with low efficiency is far from obvious. Scheme 1 can be used as a basis for discussion. Values of $f_\Delta{}^T$, the fraction of triplet states quenched by oxygen that yield singlet oxygen, have only been reported for a small percentage of the compounds studied, and measurements of $f_\Delta{}^S$ and $f_T^{O_2}$, the fraction of excited singlet states quenched by oxygen that yield singlet oxygen and that yield triplet states, respectively (see Scheme 1), are rare.

The rate constants for quenching of singlet and triplet states by oxygen, $k_S^{O_2}$ and $k_T^{O_2}$, respectively, and the fractions of triplet states quenched by oxygen that yield singlet oxygen, $f_\Delta{}^T$, 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.[1−13]

In 1992 we showed[2] for the first time a clear inverse correlation between the rate constants $k_T^{O_2}$ and the efficiency of singlet oxygen generation $f_\Delta{}^T$ from the triplet states of a range of substituted naphthalenes in benzene. The wide variation in $f_\Delta{}^T$ and $k_T^{O_2}$ values was explained by a mechanism involving the participation of charge transfer interactions, and this was supported by their dependence on ΔG^{CT}, the free energy change for charge transfer upon transfer of an electron from the triplet state of the substituted naphthalene to ground state oxygen. The evidence for the participation of charge transfer interactions is strong since the only property that varies significantly with changing substituent is the oxidation potential (E_M^{OX}) of the naphthalene derivative. This study was extended to other solvents,[3] and the inverse correlation between $f_\Delta{}^T$ and $k_T^{O_2}$ and their dependence on the oxidation potential of the naphthalene derivative was shown still to hold in the solvents used, which were acetonitrile, benzene, and cyclohexane. Solvent polarity can have a dramatic effect on both the efficiency of singlet oxygen generation, $f_\Delta{}^T$, and the quenching rate constant, $k_T^{O_2}$. For example, for 2-methoxynaphthalene $f_\Delta{}^T$ values were 0.44,

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SCHEME 1

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

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

$$ \left.\begin{array}{l} {}^1M^* + {}^3O_2 \xrightarrow{k_{S\Delta}} {}^3M^* + {}^1O_2^* \\ {}^1M^* + {}^3O_2 \xrightarrow{k_{ST}} {}^3M^* + {}^3O_2 \\ {}^1M^* + {}^3O_2 \xrightarrow{k_{SO}} \text{Quenching} \end{array}\right\} k_S^{O_2} = k_{S\Delta} + k_{ST} + k_{SO} \qquad \begin{array}{l} f_\Delta^S = k_{S\Delta}/k_S^{O_2} \\ f_T^{O_2} = (k_{S\Delta} + k_{ST})/k_S^{O_2} \\ \Phi_F^O/\Phi_F = F^o/F = 1 + k_S^{O_2}[O_2]/k_{SD} \end{array} $$

$$ \begin{aligned} P_S^{O_2} &= k_S^{O_2}[O_2]/(k_{SD} + k_S^{O_2}[O_2]) \\ &= (F^o - F)/F^o \end{aligned} $$

$$ {}^3M^* \xrightarrow{k_{TD}} {}^1M $$

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

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

0.50, and 0.80 in acetonitrile, benzene, and cyclohexane, with corresponding values for $k_T^{O_2}$ of 5.3 × 10^9, 3.5 × 10^9, and 2.4 × 10^9 dm^3 mol^{-1} s^{-1}, respectively.

Dependence of $f_\Delta{}^T$ and $k_T^{O_2}$ on the oxidation potentials for a number of substituted aromatic hydrocarbons and ketones in toluene has also been shown by Grewer and Brauer.[4] However, the dependence of their data on the free energy change for charge transfer show much more scatter than the data reported by McGarvey et al.[2] for substituted naphthalenes in benzene. This may be due to the greater variation in the nature of the compounds studied, which have, for example, different triplet energies, whereas the naphthalene derivatives have approximately the same triplet energy.

Previously, we have compared the yields of singlet oxygen production in acetonitrile and cyclohexane for a series of anthracene derivatives[5] and showed that the increase in solvent polarity causes a decrease in the quantum yield of singlet oxygen production extrapolated to infinite oxygen concentration. In acetonitrile, the oxygen quenching of the excited singlet states occurs through an additional channel, which is negligible in cyclohexane. This additional process brings about an increase in the quenching rate constant and lowers both $f_\Delta{}^S$ and $f_T^{O_2}$, the efficiencies of singlet oxygen production from singlet excited states and the efficiencies of formation of triplet states resulting from oxygen quenching of singlet states.[5] We have also showed that in acetonitrile and cyclohexane, the efficiency of singlet oxygen production from triplet states of anthracene derivatives quenched by oxygen, $f_\Delta{}^T$, is in all cases unity with the exception of 9-methoxyanthracene in acetonitrile where the value drops to one-third.[5]

Pressure effects on the dynamic quenching by oxygen of singlet and triplet states of anthracene derivatives have also been reported.[6] It has been found that the values for $k_S^{O_2}$ and $k_T^{O_2}$ decrease with increasing pressure, mainly as a result of the increase in viscosity of the solvent that accompanies the pressure increase. The ratio of $k_T^{O_2}$ to $k_S^{O_2}$ was found reasonably close to the predicted spin statistical value of 1/9 at 0.1 MPa in methylcyclohexane but less than 1/9 in *n*-butane, *n*-pentane, *n*-hexane, and *n*-heptane, and increases to >1/3 at 400 MPa for 9-acetylanthracene in all solvents. These results suggest that triplet encounter complexes take part and possibly even quintet encounter complexes may participate in the quenching mechanism as the pressure increases.

Recently, we have studied oxygen quenching of the triplet states of substituted biphenyls in acetonitrile.[7] Quenching rate constants higher than those of substituted naphthalenes were observed. Thus in the case of compounds with $E_M^{OX} = 1.3$ V (vs SCE), e.g., 4,4′dimethoxybiphenyl and 1-methoxynaphthalene, the quenching rate constants were 1.26 × 10^{10} and 7.2 × 10^9 dm^3 mol^{-1} s^{-1}, respectively; however, the efficiency of singlet oxygen production, $f_\Delta{}^T$, from both compounds was the same (0.31) and for compounds with $E_M^{OX} = 1.53 \pm 0.1$ V (vs SCE), viz., 4-methoxybiphenyl, 2-methoxynaphthalene, 1-methylnaphthalene, and 2-methylnaphthalene, the quenching rate constants, $k_T^{O_2}$ were 8.6 × 10^9, 5.3 × 10^9, 3.2 × 10^9, and 3.1 × 10^9 dm^3 mol^{-1} s^{-1} with $f_\Delta{}^T$ values of 0.36, 0.44, 0.60, and 0.61, respectively. The higher quenching rate constants and the lower values for observed $f_\Delta{}^T$ for biphenyls was attributed to the greater importance of charge transfer interactions in the former case than for naphthalenes.

This paper explores the effect of change of solvent on oxygen quenching of triplet states in the case of biphenyl derivatives to help with further understanding of the nature of the charge transfer interactions involved.

Experimental Section

Benzophenone (Aldrich, Gold Label), naphthalene (Aldrich, scintillation grade, Gold Label), 4,4′-dimethoxybiphenyl (Aldrich), 4-methylbiphenyl (Aldrich), 4-chlorobiphenyl (Lancaster, >99%) *p*-methoxyacetophenone (Aldrich), and tetrabutylammonium perchlorate (TBAP) (Fluka, >99%) were used as received. 4-Methoxybiphenyl (Aldrich 97%), 4,4′-dichlorobiphenyl (Lancaster), and 4,4′-Dibromobiphenyl (Aldrich) were recrystallized from ethanol. 4-Cyanobiphenyl (Aldrich) was vacuum sublimed. Acetonitrile (Aldrich, spectrophotometric grade) was dried by refluxing over calcium hydride. Acridine and phenazine (Aldrich) were recrystallized from methanol. Benzene (Aldrich spectrophotometric grade) and cyclohexane (Aldrich spectrophotometric and anhydrous grades) were used as received.

For singlet oxygen luminescence measurements, the third harmonic of a Lumonics Q-switched Nd:YAG laser (HY 200, 8 ns, 11 mJ) was employed as a 355 nm excitation source. Time-resolved singlet oxygen luminescence (1270 nm) was detected using a Judson Germanium photodiode (G-050, active diameter ~0.5 cm). The laser energies employed during Φ_Δ measurements did not exceed 0.5 mJ pulse^{-1}. Individual luminescence traces (16 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 intensity. The slopes obtained for these straight line plots were compared with those obtained from optically matched standards in each of the solvents, thereby yielding relative Φ_Δ values. The absorbances of the optically matched solutions were typically 0.35 at 355 nm, corresponding to benzophenone concentrations in the range (2.8−3.2) × 10^{-3} mol dm^{-3}.

The same laser was used as the excitation source for measuring the decay kinetics of triplet state absorption using a 300 W xenon arc lamp as the analyzing source. Full details of the laser flash photolysis instrument used have been given previously.[8] The rate constants $k_T^{O_2}$ for oxygen quenching of the triplet states were determined by measuring the decay of triplet−triplet absorption at the absorption maximum for each biphenyl derivative in the presence and absence of air. The pseudo-first-order decay constant in air-saturated solutions, k_{obs}, is given by

$$k_{obs} = k_{TD} + k_T^{O_2}[O_2] \qquad (1)$$

where k_{TD} is the first-order constant for decay of the triplet state absorption in the absence of air. The oxygen concentrations in air-equilibrated solvents were taken to be 1.9×10^{-3} mol dm^{-3} in acetonitrile and in benzene and 2.4×10^{-3} mol dm^{-3} in cyclohexane.[14]

Results and Discussion

To study the efficiency of singlet oxygen production during oxygen quenching of triplet states without complications due to oxygen quenching of singlet states, the indirect population of the triplet states of the biphenyl derivatives was utilized following energy transfer from a ketone ($\lambda_{ex} = 355$ nm) with 100% efficiency. It was confirmed from the measurements of absorption spectra that all of the biphenyl derivatives do not absorb at wavelengths above 310 nm. This method, which has been used previously by us[15a] and by Gorman et al.[15b] can populate the substituted biphenyl (BP) triplet state with unit efficiency by energy transfer from the aromatic ketone (K) triplet state, viz.,

$$^1K^* \xrightarrow{\Phi_T = 1} {^3K^*} \xrightarrow{BP} {^3BP^*} \xrightarrow{O_2} O_2^*(^1\Delta_g) \qquad (2)$$

The energy of the triplet state of benzophenone[16] used as the ketone sensitizer is 289 kJ mol^{-1}, and since this is ~15 kJ mol^{-1} higher than that of the highest triplet state of the biphenyls studied here, namely, 274 kJ mol^{-1} for biphenyl itself, efficient energy transfer ensues[17,18] with rate constants for energy transfer[19] $> 10^9$ dm^3 mol^{-1} s^{-1}. Experimental support for this efficient energy transfer has been confirmed by

(1) Monitoring the triplet absorption[3] 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%.

(2) Measuring the efficiency of sensitized singlet oxygen production from the triplet state of biphenyl using solutions containing a constant concentration of benzophenone (3×10^{-3} mol dm^{-3}) and different concentrations of biphenyl, extended from 6.4×10^{-3} to 8.8×10^{-2} mol dm^{-3}. The singlet oxygen luminescent intensities at time zero, I_o, were plotted against the laser intensity, the slopes obtained for these solutions of biphenyl at different concentrations were identical. This confirms 100% quenching by biphenyl at these high concentrations.

(3) Populating the triplet states of biphenyl and 4,4′-dimethoxybiphenyl following energy transfer from two different aromatic ketones, namely benzophenone and 4-methoxyacetophenone. The latter has 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.

(4) Measuring the efficiency of singlet oxygen generation from the triplet state of 4-cyanobiphenyl following energy transfer from benzophenone and 4-methoxyacetophenone in acetonitrile and showing these were the same within the experimental error (±2%), which demonstrates that although there is a considerable difference in the oxidation potentials between the 4-methoxyacetophenone and 4-cyanobiphenyl, no charge transfer quenching was observed and energy transfer from benzophenone and from 4-methoxyacetophenone to this biphenyl derivative is 100% efficient.

For Φ_Δ measurements in acetonitrile two standards have been used, the first of which, benzophenone/naphthalene,[3] has a Φ_Δ value of 0.62. This standard depends on energy transfer, and the solution has a refractive index that closely matches those of the measured solutions. The second standard used was acridine,[20] which has a Φ_Δ value of 0.82. The measured Φ_Δ values for biphenyl derivatives relative to the two standards are the same within 2%, which demonstrates that at the concentrations used for these substituted biphenyls there is no need to apply corrections for the small refractive index changes present under our experimental conditions. In benzene we used two standards. The first is benzophenone/naphthalene[2] with $\Phi_\Delta =$ 0.62, and the second is phenazine[3] with $\Phi_\Delta = 0.83$; again, the measured values of Φ_Δ for biphenyl derivatives relative to the two standards were the same within 2%. In cyclohexane we have used as constant standards $\Phi_\Delta = 0.92$ for benzophenone/naphthalene as determined by Gorman et al.[21] and phenazine $\Phi_\Delta = 0.96$ as determined by Wilkinson et al.[3] Figure 1 shows the dependence of singlet oxygen luminescence I_o at $t = 0$, on the laser intensity for some biphenyl derivatives in benzene (Figure 1A) and in cyclohexane (Figure 1B).

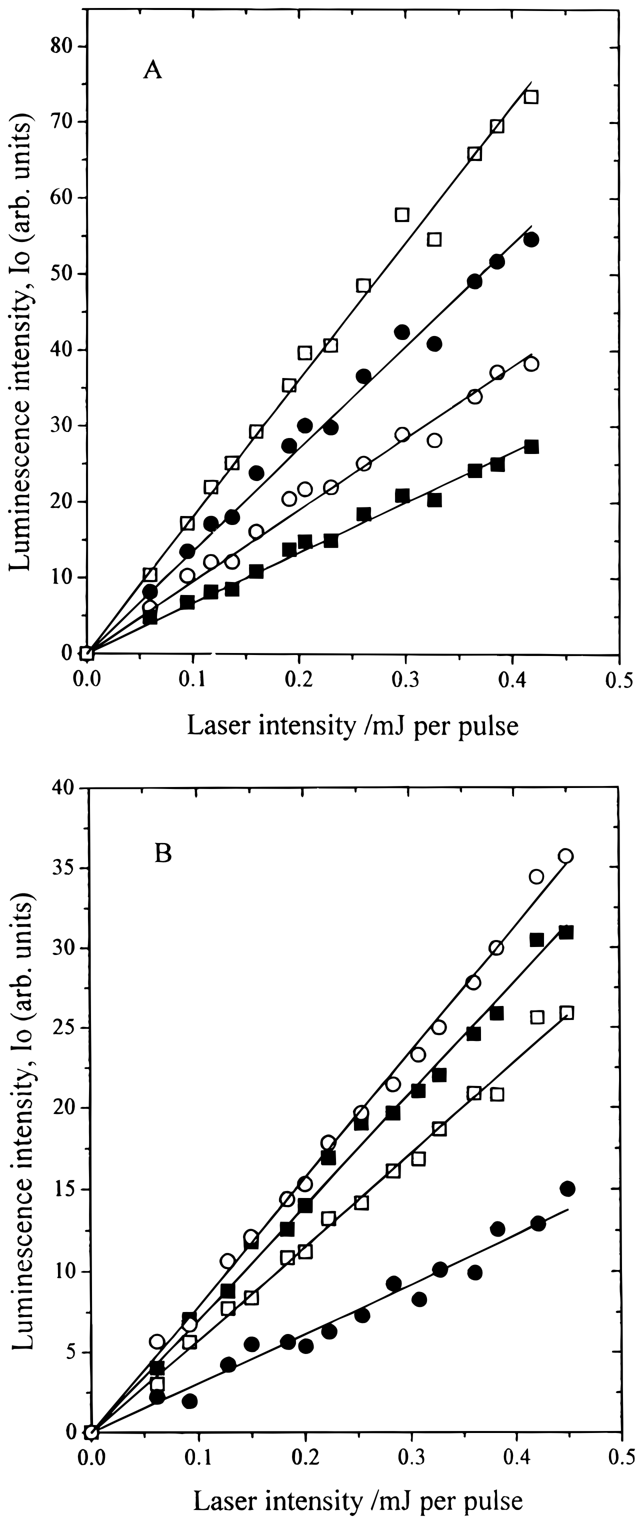

Figure 1. Dependence on laser fluence of the initial luminescence intensity, I_o, due to singlet oxygen phosphorescence following laser excitation of optically matched solutions of benzophenone in (A) benzene containing 4-cyanobiphenyl (□), 4-bromobiphenyl (●), 4-methylbiphenyl (○), and 4-methoxybiphenyl (■) and in (B) cyclohexane containing 4-cyanobiphenyl (○), 4-chlorobiphenyl (■), 4-methylbiphenyl (□), and 4-methoxybiphenyl (●).

The quantum yield of singlet oxygen production (Φ_Δ) arising from the triplet state quenching is given by

$$\Phi_\Delta = \Phi_T P_T^{O_2} f_\Delta{}^T \tag{3}$$

where Φ_T is the quantum yield of triplet state production of the molecule of interest under the conditions of the experiment, $P_T^{O_2}$, is the fraction of triplet states quenched by oxygen, and $f_\Delta{}^T$ is the fraction of these triplet states quenched by oxygen that yield $O_2{}^*({}^1\Delta_g)$. Since the method employed results in $\Phi_T = 1$, Φ_Δ will be given by

$$\Phi_\Delta = P_T^{O_2} f_\Delta{}^T \tag{4}$$

and $P_T^{O_2}$ can be calculated using the following equation

$$P_T^{O_2} = \frac{k_T^{O_2}[O_2]}{k_{TD} + k_T^{O_2}[O_2]} \tag{5}$$

For all these biphenyl derivatives $P_T^{O_2}$, equals 1.0 (within experimental error, 2%), except in the case of 4,4′-dichlorobiphenyl where $P_T^{O_2}$, values of 0.75, 0.61, and 0.79 in acetonitrile, benzene, and cyclohexane, respectively, were obtained (Table 1).

The quantum yields of singlet oxygen production were found to be constant (i.e., within 3%) over a wide range of concentrations used for these experiments. The decay rate constants k_Δ of $O_2{}^*({}^1\Delta_g)$ in the solvents used were in agreement with those in the literature[3,22−25] for all compounds, except as given below, being 1.25(±0.1) × 10^4 s^{-1} in acetonitrile, 3.2(±0.2) × 10^4 s^{-1} in benzene, and 4.2(±0.2) × 10^4 s^{-1} in cyclohexane. However, the rate constants for singlet oxygen decay in acetonitrile were found to be higher when sensitized by using increasing concentrations of 4,4′-dimethoxybiphenyl and 4-methoxybiphenyl. Stern−Volmer plots were used to measure the quenching rate constant of singlet oxygen by 4,4′-dimethoxybiphenyl and 4-methoxybiphenyl, and values obtained were 3.4(±0.3) × 10^5 and 3.1(±0.3) × 10^5 $dm^3\ mol^{-1}\ s^{-1}$, respectively.

Taylor et al.[26] measured the energies of the triplet state for 16 biphenyl derivatives substituted at 4 and 4,4′ positions in EPA and they found that upon substitution the energy difference between the first excited triplet state and the singlet ground state, $E(S_0 - T_1)$, does not change much and follows the same trend as $E(S_0 - S_1)$. In addition, Dreeskamp et al.[27] carried out a similar study on the effect of chlorosubstitution on the electronic spectra of biphenyl derivatives. They found that the triplet energy for both mono- and di-para-substituted compounds are approximately equal (264 ± 4 kJ mol^{-1}). Recently, Naik et al.[17,28] reported the triplet state energies for some 4,4′-disubstituted biphenyls in benzene. We have also measured the triplet energies and find they all lie in the range 265−274 kJ mol^{-1}, in agreement with Taylor et al.,[26] Dreeskamp et al.,[27] and Naik et al.[17,28]

Changing the nature of the substituent on the biphenyl ring affects the oxidation potential of these compounds and thereby ΔG^{CT}. A good estimate for the free energy change (ΔG^{CT}) to form ion pairs from excited states with energy E_T as shown by Rehm and Weller[29] is given by

$$\Delta G^{CT} = F[E_M^{OX} - E_{O_2}^{red}] - E_T + C \tag{6}$$

where F is the Faraday constant, $E_{O_2}^{red}$ is the half-wave reduction potential for oxygen (−0.78 V vs SCE[30]), and C is the electrostatic interaction energy, which is inversely proportional to the static relative permittivity of the solvent, ϵ_r. Table 1 shows the measured values for $k_T^{O_2}$, $P_T^{O_2}$, and $f_\Delta{}^T$ together with the free energy change ΔG^{CT} calculated from eq 6 taking $C = 0$ using our measured values[7] of the half-wave oxidation potentials and triplet energies of the substituted biphenyls.

TABLE 1: Rate Constants $k_T^{O_2}$ and Singlet Oxygen Formation Efficiencies $f_\Delta{}^T$ for Oxygen Quenching of the Triplet States of Biphenyl Derivatives in (A) Acetonitrile, (B) Benzene, and (C) Cyclohexane[a]

sensitizer	$k_T^{O_2}$ (10^9 dm^3 mol^{-1} s^{-1})[b] A[c]	B	C	$f_\Delta{}^T$ A[c]	B	C	E_T (±1.0) (kJ mol^{-1})	E_M^{OX} (±0.02)[c] (V vs SCE)	ΔG^{CT} (kJ mol^{-1})
4,4′-dimethoxybiphenyl	12.60	9.15		0.31 ± 0.03	0.31 ± 0.04		266	1.30	−65.31
4-methoxybiphenyl	8.56	5.94	2.67	0.36 ± 0.03	0.29 ± 0.06	0.37 ± 0.04	270	1.53	−47.12
4,4′-dimethylbiphenyl	5.93	3.71	1.50	0.42 ± 0.04	0.37 ± 0.04	0.62 ± 0.06	269	1.69	−30.68
4-methylbiphenyl	4.36	2.46	1.12	0.44 ± 0.04	0.41 ± 0.41	0.70 ± 0.07	272	1.80	−23.06
biphenyl	2.85	1.51	0.78	0.48 ± 0.04	0.51 ± 0.05	0.75 ± 0.07	274	1.91	−14.45
4-chlorobiphenyl	2.10	1.36	0.76	0.56 ± 0.05	0.61 ± 0.06	0.85 ± 0.08	269	1.96	−4.63
4-bromobiphenyl	2.05	1.35	0.71	0.59 ± 0.06	0.61 ± 0.06	0.89 ± 0.09	266	1.95	−2.59
4,4′-dichlorobiphenyl[d]	1.77	1.00	0.90	0.58 ± 0.06	0.89 ± 0.10	0.83 ± 0.08	265	2.02	5.16
4,4′-dibromobiphenyl	1.46	1.07	0.66	0.67 ± 0.07	0.71 ± 0.07	0.92 ± 0.10	265	2.01	4.19
4-cyanobiphenyl	0.88	0.82	0.43	0.84 ± 0.08	0.79 ± 0.08	0.96 ± 0.10	265	2.11[e]	13.8

[a] Energy of the triplet state, E_T, measured from the phosphorescence emission in ethanol glass (77 K), the half-wave oxidation potentials, E_M^{OX}, in acetonitrile, and free energy change for charge transfer, ΔG^{CT}, from eq 6 with $C = 0$. [b] Error 10%. [c] Reference 7. [d] $P_T^{O_2} = 0.75$, 0.61, and 0.79 in acetonitrile, benzene, and cyclohexane, respectively. [e] ±0.05.

It is clear from Table 1 and Figure 2 that there is an inverse correlation between $f_\Delta{}^T$ and $k_T^{O_2}$ for all of the compounds studied in the three solvents. Table 1 shows that there is a strong dependence of $f_\Delta{}^T$ and $k_T^{O_2}$ on the half-wave oxidation potential, E_M^{OX}. Thus compounds with electron-donating groups (methoxy and methyl groups) show high quenching rate constants and low efficiency of singlet oxygen production, whereas compounds with electron-withdrawing groups (halogen atoms or cyano groups) show the opposite trend.

The quenching of triplet states by molecular oxygen can be described[7,31] by Scheme 2 based on that originally proposed by Gijzman et al.,[32] who, from their studies of the oxygen quenching of triplet states of unsubstituted aromatic hydrocarbons, concluded step b was negligible.

SCHEME 2

$$\begin{aligned}
&\underset{k_{-d}}{\overset{1/9k_d}{\rightleftarrows}}\ {}^1({}^3M^{*}...O_2,{}^3\Sigma_g{}^-)^{*} \xrightarrow{k_{et}} {}^1(M^{+}...O_2{}^-) \rightarrow M + O_2{}^{*}({}^1\Delta_g) \quad (a)\\
{}^3M^{*} + O_2({}^3\Sigma_g{}^-)\ &\underset{k_{-d}}{\overset{3/9k_d}{\rightleftarrows}}\ {}^3({}^3M^{*}...O_2,{}^3\Sigma_g{}^-)^{*} \xrightarrow{k_{ic}} {}^3(M^{+}...O_2{}^-) \rightarrow M + O_2({}^3\Sigma_g{}^-) \quad (b)\\
&\underset{k_{-d}}{\overset{5/9k_d}{\rightleftarrows}}\ {}^5({}^3M^{*}...O_2,{}^3\Sigma_g{}^-)^{*}
\end{aligned}$$

Here k_d is the bimolecular diffusion-controlled rate constant and k_{-d} is the unimolecular rate constant for separation of the encounter pairs to original reactants.

According to Scheme 2

$$k_T^{O_2} = (k_d/9)[k_{et}/(k_{et} + k_{-d})] + (3k_d/9)[k_{ic}/(k_{ic} + k_{-d})] \quad (7)$$

and

$$f_\Delta{}^T = (k_d/9)[k_{et}/(k_{et} + k_{-d})]/k_T^{O_2} \quad (8)$$

Equation 8 explains partially the inverse correlation between $f_\Delta{}^T$ and $k_T^{O_2}$ (Figure 2).

Several workers[3,4,6,7,31,33,34] have reported rate constants for oxygen quenching of triplets states well in excess of $k_d/9$, and this is the case for the $k_T^{O_2}$ values given in Table 1 for 4,4′-dimethoxybiphenyl in acetonitrile and in benzene. For a discussion of $k_T^{O_2}$ values see ref 18. To account for $k_T^{O_2}$ values higher than $k_d/9$, Garner and Wilkinson[31] suggested the involvement of charge transfer complexes in the mechanism of quenching by molecular oxygen. In all three solvents it is apparent (see Figure 3) that $k_T^{O_2}$ exhibits an inverse dependence on ΔG^{CT} calculated from eq 6 by taking $C = 0$. In the case of acetonitrile $\epsilon_r = 37$, and the term C can be neglected.[7,35] For benzene and cyclohexane $\epsilon_r = 2.284$ and 2.023, respectively,[14] which means that the term C becomes more important and cannot be neglected in these two solvents (see later). The solvent effect on the quenching rate constants is shown in Figure 3.

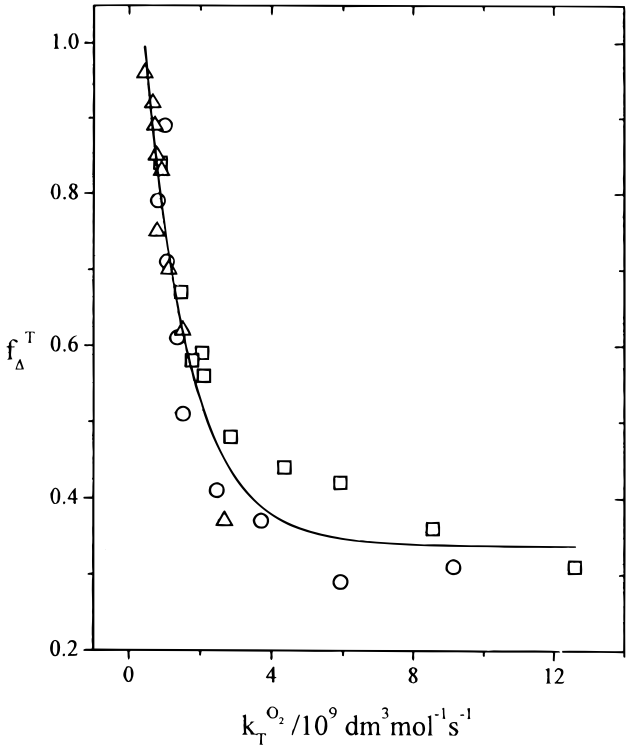

Figure 2. Dependence of the efficiency of $O_2{}^{*}({}^1\Delta_g)$ production, $f_\Delta{}^T$, on the rate constant for quenching of triplet state by oxygen, $k_T^{O_2}$, for substituted biphenyls in acetonitrile (□), benzene (○), and cyclohexane (△).

From eq 7 we expect $k_T^{O_2}$ values that are close to one-ninth of the diffusion-controlled rate constant to be sensitive to changes in viscosity. To interpret the results in Table 1, it is interesting to calculate the appropriate values of k_d, the diffusion-controlled rate constants in different solvents, using eq 9:[36]

$$k_d = 4\pi N(D_{BP} + D_{O_2})(r_{BP} + r_{O_2}) \quad (9)$$

where r_{BP} is considered to be 0.4 nm and r_{O_2} is taken as 0.2

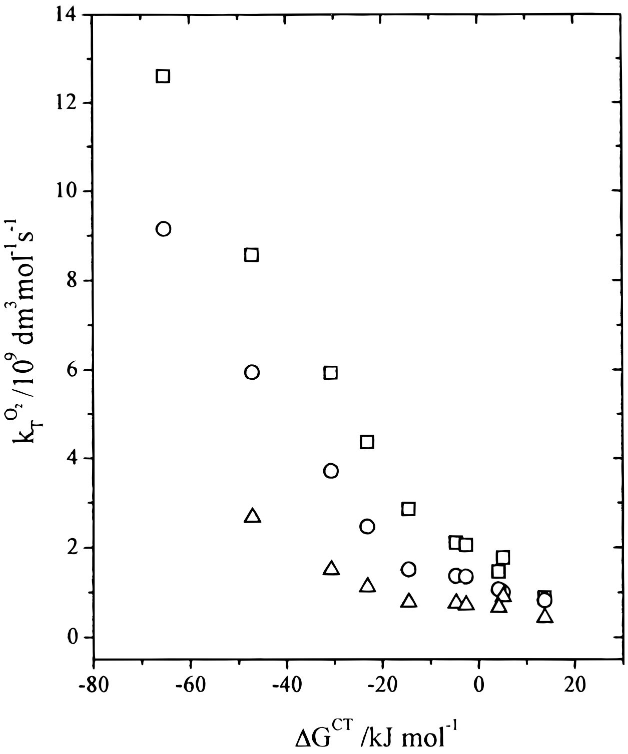

Figure 3. Dependence of the rate constant for quenching of the triplet state by oxygen, $k_T^{O_2}$, on the free energy change, ΔG^{CT}, for charge transfer from $^3M^*$ to $O_2(^3\Sigma_g^-)$ for substituted biphenyls in acetonitrile (□), benzene (○), and cyclohexane (△), assuming the term *C* of eq 6 is zero in all solvents.

nm.[24] The diffusion coefficients of oxygen have been measured in different solvents by different groups.[36−38] Values of D_{O_2} in acetonitrile and benzene have been reported to be 7.12(±0.64) × 10^{-5} cm^2 s^{-1} [37,38] and 5.7 × 10^{-5} cm^2 s^{-1},[36] respectively. We estimate D_{O_2} in cyclohexane to be 4.86(±0.2) × 10^{-5} cm^2 s^{-1} from a plot of measured D_{O_2} versus $1/\eta$, where η is the viscosity coefficient of the different solvents. Diffusion coefficients of biphenyl have been measured in different solvents by Miller et al.[39] A plot of D_{BP} versus $1/\eta$ gives a very good straight line, from which D_{BP} was obtained for the solvents used in this work. The obtained values of D_{BP} were 2.81 × 10^{-5}, 1.65 × 10^{-5}, and 1.13 × 10^{-5} cm^2 s^{-1} in acetonitrile, benzene, and cyclohexane, respectively, at 25 °C. Incorporation of these data into eq 9 results in k_d values of 4.50 × 10^{10}, 3.33 × 10^{10}, and 2.72 × 10^{10} dm^3 mol^{-1} s^{-1} in acetonitrile, benzene, and cyclohexane, respectively. In the discussion of our previous work[3] on the effect of these solvents on $k_T^{O_2}$ values for naphthalene and its derivatives we used k_d values quoted by Darmanyan and Foote[40,41] of 3.7 × 10^{10} dm^3 mol^{-1} s^{-1} in acetonitrile and 3.0 × 10^{10} dm^3 mol^{-1} s^{-1} in benzene and cyclohexane. However, Kristiansen et al.[22] have measured $k_S^{O_2}$, the quenching rate constants of the excited singlet state of biphenyl by molecular oxygen, in acetonitrile and cyclohexane at 25 °C and report values of 4.3 ± 0.6 and 2.6 ± 0.2 × 10^{10} dm^3 mol^{-1} s^{-1}, respectively. On the basis of the agreement of the values calculated from eq 9 with the two experimental values,[22] which should be less than or equal to k_d, we have used these values calculated from eq 9 for k_d in the further discussion.

Based on Scheme 2 the value of the efficiency of singlet oxygen generation from the triplet state would be 1.0 if only the singlet channel (channel a in Scheme 2) were involved and 0.25 if the singlet and the triplet channels (channels a and b in Scheme 2) were both involved equally, e.g., both diffusion controlled when $k_T^{O_2}$ would be $4k_d/9$. However, neither of these limiting values has been observed for the range of compounds studied here. For example, in acetonitrile and benzene, compounds with half-wave oxidation potentials >1.91 V vs SCE, have quenching rate constants $<k_d/9$ and the observed f_Δ^T values lie in the range 0.50−0.84, which is far from unity. In cyclohexane the quenching rate constants are less than $k_d/9$ for all compounds, and f_Δ^T values only approach unity for compounds with high oxidation potentials. Such behavior can be attributed to enhanced intersystem crossing between the charge transfer states or to the triplet channel being important even when $k_T^{O_2} < k_d/9$.

In Figure 4 a plot is shown of f_Δ^T against $k_T^{O_2}/k_d$ using the calculated values of k_d in the different solvents. Figure 5 shows a plot of $k_T^{O_2}/k_d$ versus ΔG^{CT} in which we have used the *C* term of eq 6 equal to 0.0, 3.0, and 20.0 kJ mol^{-1} for acetonitrile, benzene, and cyclohexane, respectively. These values were obtained by examination of plots using different values for *C*, and the best overlap was found with the acetonitrile data taking *C* equal to 3 ± 2 kJ mol^{-1} in benzene and 20 ± 3 kJ mol^{-1} in cyclohexane (cf. ref 35 where a value of $C \approx 0$ is used for benzene as solvent). The dependences of $k_T^{O_2}$ and $k_T^{O_2}/k_d$ on ΔG^{CT} shown in Figures 3 and 5, respectively, are good evidence for the involvement of charge transfer interactions in the quenching process. The following equations can be used to calculate the rate constants for quenching via the singlet channel, resulting in energy transfer to oxygen and quenching via the triplet channel in Scheme 2, respectively. Equations 10 and 11 define these net rate constants as $k_q{}^1$ for the singlet pathway and $k_q{}^3$ for the triplet pathway, viz.

$$k_q{}^1 = k_T^{O_2} f_\Delta{}^T \tag{10}$$

$$k_q{}^3 = k_T^{O_2}(1 - f_\Delta{}^T) \tag{11}$$

The knowledge of $k_q{}^1$ and $k_q{}^3$ allows the calculation of the quenching probabilities for the singlet channel p_1 and the triplet channel p_3, according to Scheme 2,

$$p_1 = \frac{k_{et}}{k_{-d} + k_{et}} = \frac{9}{k_d} k_q{}^1 \tag{12}$$

$$p_3 = \frac{k_{ic}}{k_{-d} + k_{ic}} = \frac{3}{k_d} k_q{}^3 \tag{13}$$

and

$$\frac{p_1}{1 - p_1} = \frac{k_{et}}{k_{-d}} \tag{14}$$

$$\frac{p_3}{1 - p_3} = \frac{k_{ic}}{k_{-d}} \tag{15}$$

k_d is taken to be equal to 4.50 × 10^{10}, 3.33 × 10^{10}, and 2.72 × 10^{10} dm^3 mol^{-1} s^{-1} in acetonitrile, benzene, and cyclohexane, respectively. The experimental values of $k_q{}^1$, $k_q{}^3$, k_{et}/k_{-d}, and k_{ic}/k_{-d} are listed in Tables 2 and 3.

When $\log(k_{ic}/k_{-d})$ and $\log(k_{et}/k_{-d})$ are plotted versus ΔG^{CT} (Figure 6A,B), a good linear dependence is observed for the triplet channel with slopes of −0.022, −0.027, and −0.030 mol/kJ in acetonitrile, benzene, and cyclohexane, respectively, compared with an expected slope of −0.178 mol/kJ for reactions involving complete electron transfer.[42] This can be interpreted as the percentage electron transfer in the transition state being

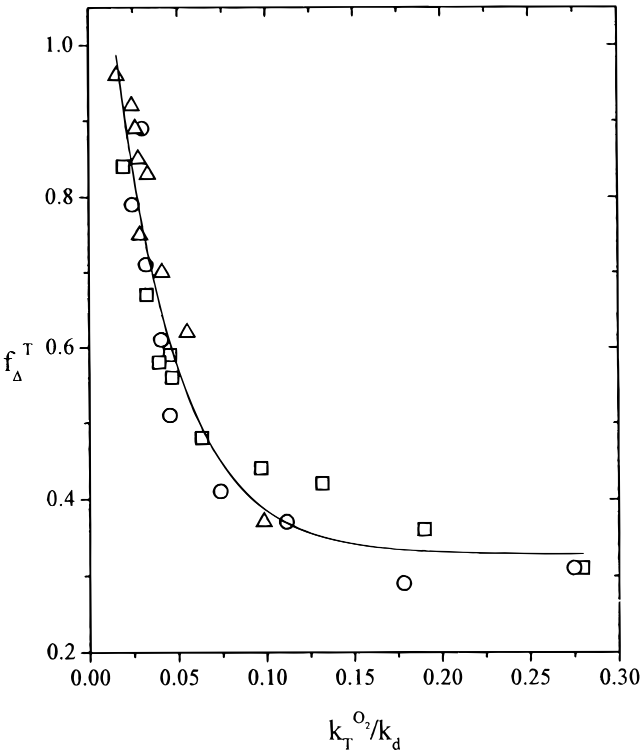

Figure 4. Dependence of the efficiency of $O_2*(^1\Delta_g)$ production, f_Δ^T, on $k_T^{O_2}/k_d$ where k_d is the solvent dependent bimolecular rate constant at the diffusion limit (see text): (□) in acetonitrile, (○) in benzene, and (△) in cyclohexane.

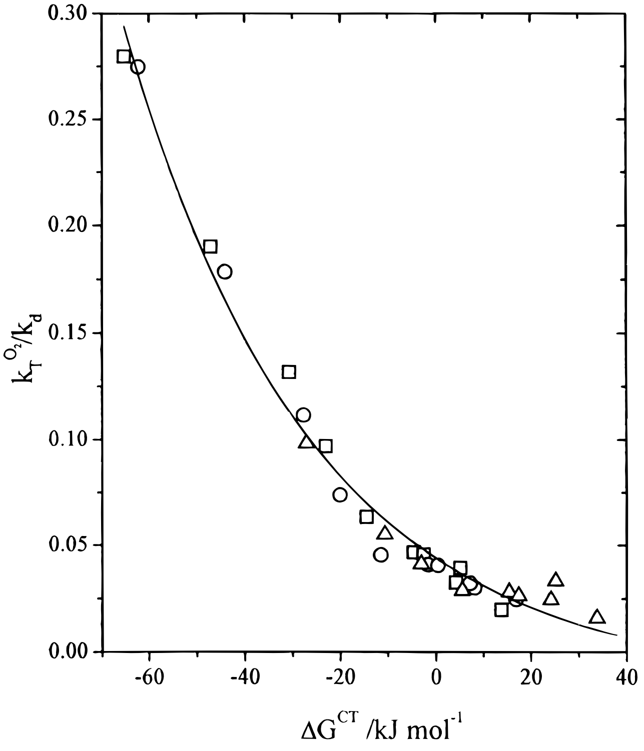

Figure 5. Dependence of $k_T^{O_2}/k_d$ on the free energy change ΔG^{CT} (see eq 6): (□) in acetonitrile, (○) in benzene, and (△) in cyclohexane. The electrostatic interaction energy, *C* in eq 6, is considered as negligible in the case of acetonitrile and considered as 3.0 kJ mol^{-1} in the case of benzene and 20.0 kJ mol^{-1} in case of cyclohexane.

TABLE 2: k_{et}/k_{-d} and k_{ic}/k_{-d} for Biphenyl Derivatives Calculated from Eqs 14 and 15 in Acetonitrile, Benzene, and Cyclohexane

	acetonitrile		benzene		cyclohexane	
sensitizer	k_{et}/k_{-d}	k_{ic}/k_{-d}	k_{et}/k_{-d}	k_{ic}/k_{-d}	k_{et}/k_{-d}	k_{ic}/k_{-d}
4,4′-dimethoxybiphenyl	3.57	1.38	2.87	1.36		
4-methoxybiphenyl	1.61	0.58	0.87	0.61	0.49	0.23
4,4′-dimethylbiphenyl	0.99	0.30	0.59	0.27	0.44	0.07
4-methylbiphenyl	0.62	0.19	0.37	0.15	0.35	0.04
biphenyl	0.38	0.11	0.26	0.07	0.24	0.02
4-chlorobiphenyl	0.31	0.07	0.29	0.05	0.27	0.01
4-bromobiphenyl	0.32	0.06	0.29	0.05	0.27	0.01
4,4′-dichlorobiphenyl	0.26	0.05	0.32	0.01	0.33	0.02
4,4′-dibromobiphenyl	0.24	0.03	0.26	0.03	0.25	0.01
4-cyanobiphenyl	0.17	0.01	0.21	0.02	0.16	0.00

12.4%, 15.2%, and 16.9% in acetonitrile, benzene, and cyclohexane, respectively, independent of the substituent for the triplet channel. The fact that the more polar solvent shows a smaller fractional charge transfer is surprising (see later). The linear fit for the singlet channel Figure 6B is not as good as for the triplet channel because, even when ΔG^{CT} is positive, quenching is relatively efficient and thus charge transfer assisted quenching is not in this case the sole contribution leading to quenching. This is allowed for in Scheme 3 by proposing a competing pathway in the singlet channel that yields singlet oxygen without assisted charge transfer, i.e., by including the extra step labeled $^1k_\Delta$ in the singlet pathway. We have also included in Scheme 3 the possibility of intersystem crossing between singlet and triplet charge transfer complexes labeled k_{ST} and k_{TS}.

In an attempt to fit the experimental data of $k_q{}^1$ and $k_q{}^3$, we have employed the equations derived from Scheme 3, which has been developed by us.[7] Thus, Scheme 3, where for simplicity $^{1,3}E$ and $^{1,3}C$ are used to represent the encounter and charge transfer complexes shown in Scheme 2, respectively, and ^1P and ^3P represent the precursor/encounter complexes $^1(M...O_2*, {}^1\Delta_g)$ and $^3(M...{}^3O_2, {}^3\Sigma_g{}^-)$, respectively. Scheme 3 incorporates Scheme 2 and includes the possibility of direct production of $O_2*(^1\Delta_g)$ without passing through the charge transfer complex ^1C; i.e., Schemes 2 and 3 are identical when $^1k_\Delta$, k_{ST}, and k_{TS} are negligibly small. If decay constants for the encounter and charge transfer complexes are defined as

$$^1k_E = k_{-d} + {}^1k_T + {}^1k_\Delta, \qquad {}^3k_E = k_{-d} + {}^3k_T$$

$$^1k_C = {}^1k_{-T} + {}^1k_p + k_{ST}, \qquad {}^3k_C = {}^3k_{-T} + {}^3k_p + k_{TS}$$

applying the steady state treatment to the reactive intermediates in Scheme 3 gives

$$k_q{}^1 = k_d\{({}^1k_T{}^1k_P + {}^1k_C{}^1k_\Delta)({}^3k_E{}^3k_C - {}^3k_T{}^3k_{-T}) + 3{}^3k_Tk_{TS}({}^1k_E{}^1k_P + k_{TS}{}^1k_\Delta) - {}^3k_Ek_{ST}k_{TS}{}^1k_\Delta)\}/9D \quad (16)$$

and

$$k_q{}^3 = k_d{}^3k_P\{3{}^3k_T({}^1k_E{}^1k_C - {}^1k_T{}^1k_{-T}) + {}^3k_E{}^1k_Tk_{ST}\}/9D \quad (17)$$

where

$$D = ({}^1k_E{}^1k_C - {}^1k_T{}^1k_{-T})({}^3k_E{}^3k_C - {}^3k_T{}^3k_{-T}) - {}^1k_E{}^3k_Ek_{ST}k_{TS} \quad (18)$$

Equations 16 and 17 simplify when k_{ST} and $k_{TS} = 0$ to give

$$k_q{}^1 = k_d({}^1k_T{}^1f_P + {}^1k_\Delta)/9(k_{-d} + {}^1k_T{}^1f_P + {}^1k_\Delta) \quad (19)$$

$$k_q{}^3 = 3k_d{}^3k_T{}^3f_P/9(k_{-d} + {}^3k_T{}^3f_P) \quad (20)$$

where $^1f_P = {}^1k_p/({}^1k_{-T} + {}^1k_P)$ and $^3f_P = {}^3k_P/({}^3k_{-T} + {}^3k_P)$; i.e., ^1f_P

TABLE 3: Experimental Values for $k_q^1 = k_T^{O_2} f_\Delta^T$ and $k_q^3 = k_T^{O_2}(1 - f_\Delta^T)$ in Acetonitrile, Benzene, and Cyclohexane[a]

	acetonitrile		benzene		cyclohexane	
sensitizer	k_q^1(k_q^1 cal)/ 10^9 dm^3 mol^{-1} s^{-1}	k_q^3(k_q^3 cal)/ 10^9 dm^3 mol^{-1} s^{-1}	k_q^1(k_q^1 cal)/ 10^9 dm^3 mol^{-1} s^{-1}	k_q^3(k_q^3 cal)/ 10^9 dm^3 mol^{-1} s^{-1}	k_q^1(k_q^1 cal)/ 10^9 dm^3 mol^{-1} s^{-1}	k_q^3(k_q^3 cal)/ 10^9 dm^3 mol^{-1} s^{-1}
4,4′-dimethoxybiphenyl	3.91 (4.07)	8.69 (8.97)	2.75 (2.86)	6.41 (6.97)		
4-methoxybiphenyl	3.08 (3.29)	5.48 (5.59)	1.72 (2.09)	4.22 (4.09)	0.99 (1.06)	1.68 (1.49)
4,4′-dimethylbiphenyl	2.49 (2.41)	3.44 (3.09)	1.37 (1.39)	2.34 (2.02)	0.93 (0.77)	0.57 (0.54)
4-methylbiphenyl	1.92 (2.02)	2.44 (2.25)	1.01 (1.15)	1.45 (1.38)	0.78 (0.71)	0.33 (0.33)
biphenyl	1.37 (1.61)	1.48 (1.54)	0.77 (0.95)	0.74 (0.88)	0.59 (0.66)	0.20 (0.19)
4-chlorobiphenyl	1.18 (1.23)	0.92 (0.97)	0.83 (0.79)	0.53 (0.51)	0.65 (0.63)	0.11 (0.10)
4-bromobiphenyl	1.21 (1.16)	0.84 (0.88)	0.82 (0.77)	0.53 (0.46)	0.64 (0.63)	0.08 (0.08)
4,4′-dichlorobiphenyl	1.03 (0.94)	0.74 (0.53)	0.89 (0.70)	0.11 (0.30)	0.75 (0.62)	0.15 (0.05)
4,4′-dibromobiphenyl	0.98 (0.96)	0.48 (0.58)	0.76 (0.71)	0.31 (0.31)	0.61 (0.62)	0.05 (0.05)
4-cyanobiphenyl	0.74 (0.75)	0.14 (0.10)	0.65 (0.65)	0.17 (0.18)	0.41 (0.61)	0.02 (0.02)

[a] Calculated values are obtained from eqs 16 and 17 using the parameters given in Table 4.

SCHEME 3

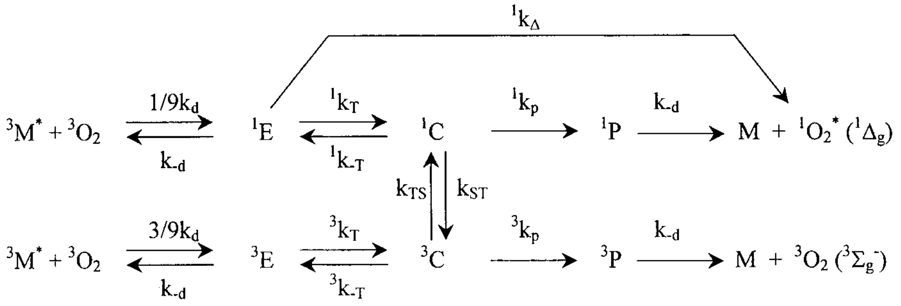

TABLE 4: Values of Different Parameters Used in Eqs 16 and 17 to Calculate k_q^1 and k_q^3 Given in Table 3 and Solid Lines Shown in Figure 7A−C

		acetonitrile	benzene	cyclohexane
$k_d/10^{10}$ dm^3 mol^{-1} s^{-1}		4.5	3.33	2.72
k_d/k_{-d}/(dm^3 mol^{-1})		1.0	1.0	1.0
^1k_T/s^{-1}		$kT/h \exp(-\Delta G_S^\ddagger/RT)$	$kT/h \exp(-\Delta G_S^\ddagger/RT)$	$kT/h \exp(-\Delta G_S^\ddagger/RT)$
^3k_T/s^{-1}		$kT/h \exp(-\Delta G_T^\ddagger/RT)$	$kT/h \exp(-\Delta G_T^\ddagger/RT)$	$kT/h \exp(-\Delta G_T^\ddagger/RT)$
$^1k_{-T}$/s^{-1}		$kT/h \exp(-(\Delta G^{CT} - \Delta G_S^\ddagger)/RT)$	$kT/h \exp(-(\Delta G^{CT} - \Delta G_S^\ddagger)/RT)$	$kT/h \exp(-(\Delta G^{CT} - \Delta G_S^\ddagger)/RT)$
$^3k_{-T}$/s^{-1}		$kT/h \exp(-(\Delta G^{CT} - \Delta G_T^\ddagger)/RT)$	$kT/h \exp(-(\Delta G^{CT} - \Delta G_T^\ddagger)/RT)$	$kT/h \exp(-(\Delta G^{CT} - \Delta G_T^\ddagger)/RT)$
$\Delta G_S^\ddagger = \alpha + \beta\ \Delta G^{CT}$	α/kJ mol^{-1} [a]	16.0	19.0	21.0
	β(b)	0.125	0.145	0.17
$\Delta G_T^\ddagger = \alpha + \beta \Delta G^{CT}$	α/kJ mol^{-1} [a]	19.3	20.6	22.0
	β[b]	0.125	0.145	0.17
^1k_p/s^{-1}		10^{12}(c)	10^{14} [d]	10^{14}
^3k_p/s^{-1}		10^{11}	10^{14} [d]	10^{14}
$^1k_\Delta$/s^{-1}		5×10^9	6×10^9	6.75×10^9
$k_{ST} = k_{TS}$/s^{-1}		$\leq 10^{11}$	$\leq 10^{12}$	$\leq 10^{13}$

[a] ±1.0. [b] ±0.005. [c] ^1k_p could be 10^{14} s^{-1} when $^1k_\Delta = 3 \times 10^9$ s^{-1}. [d] Values in the range of 10^{12}−10^{14} s^{-1} give a good fit.

and ^3f_P are the fractions of the charge transfer complexes that dissociate to give $O_2^*(^1\Delta_g)$ and $O_2(^3\Sigma_g^-)$, respectively.

Equations 16−18 have been used to calculate values of k_q^1 and k_q^3, and the best fit values are given in Table 3, which compare well with the experimental values (see also Figure 7A−C). The values of k_d are taken to be equal to 4.50×10^{10}, 3.33×10^{10}, and 2.72×10^{10} dm^3 mol^{-1} s^{-1} in acetonitrile, benzene, and cyclohexane, respectively, and k_d/k_{-d} was assumed[3] to equal 1 dm^3 mol^{-1} (see Table 4). The variable parameters used to arrive at best fits were kept to a minimum, and these parameters are listed in Table 4. Figure 7 clearly demonstrates that one set of parameters can be used to fit all 10 biphenyl derivatives in one solvent, and only slight variations are necessary to allow for changes in viscosity and polarity to give excellent fits in all three solvents using the mechanism shown in Scheme 3. It has been found that, to fit the data, it is necessary to use linear and not nonlinear free energy relationships between the free energy of activation for oxygen quenching, $\Delta G^\ddagger$, and ΔG^{CT}, as expected from the linear plot shown in Figure 6A. The linear free energy relationship, $\Delta G^\ddagger = \alpha + \beta\Delta G^{CT}$, is used, and the value of β can be interpreted as representing the fraction of electron transfer that exists in the transition state. N.B. the same value of β can be used for both ^{1}C and ^{3}C in the same solvent and β increases from 0.125 to 0.145 to 0.17 on going from acetonitrile to benzene to cyclohexane. This agrees well with our earlier finding based on the slopes of the linear plots shown in Figure 6A. Values of k_d/k_{-d} = [M] dm^3 mol^{-1}, where [M] is the solvent molarity,[18] also have been used to calculate best fit values for k_q^1 and k_q^3. Despite this large change in k_{-d}, the agreement with experiment is equally good, the values of β are unchanged but relatively lower values of α are needed to fit the data. The percentage charge transfer in the transition state represents a small fraction of electron transfer, and that fraction increases in the less polar solvent. This indicates that the transition state for the charge transfer assisted quenching is closer in nature to the nonpolar encounter complexes ^{1,3}E than to the charge transfer intermediates ^{1}C or ^{3}C. In cyclohexane the charge transfer state is 20 kJ mol^{-1} higher (C = 20 kJ mol^{-1}) than in acetonitrile, and a higher value of β in cyclohexane indicates the intersection between potential energy curves at the transition state on going

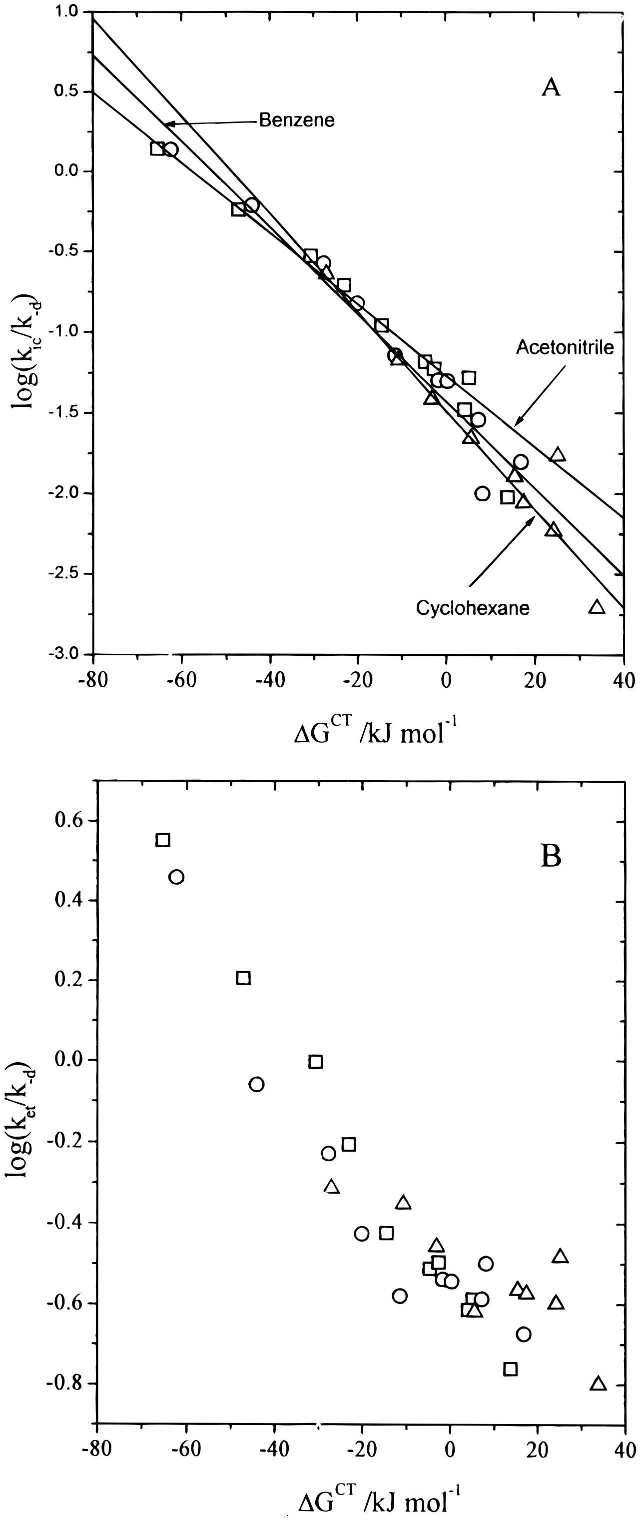

Figure 6. Plots showing (A) the dependence of $\log(k_{ic}/k_{-d})$ on the free energy change, ΔG^{CT}, and (B) the dependence of $\log(k_{et}/k_{-d})$ on the free energy change, ΔG^{CT}: (□) in acetonitrile, (○) in benzene, and (△) in cyclohexane.

from the nonpolar encounter complexes to the charge transfer complexes occurs later in cyclohexane compared with acetonitrile to give a slightly higher value of β (0.17 as compared to 0.125, see Figure 8).

Parts A−C of Figure 7 show graphically the best fit for k_q^1 and k_q^3 using the above-mentioned parameters in acetonitrile, benzene, and cyclohexane. The individual results are listed in Table 3. The lower values of ^1k_p and ^3k_p in acetonitrile than in

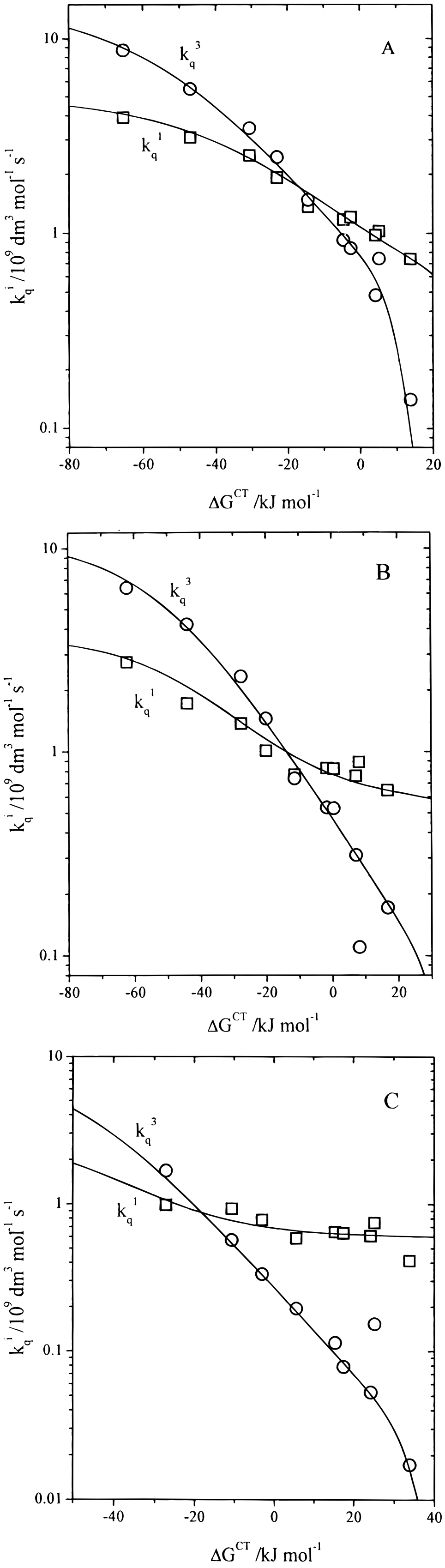

Figure 7. Plots showing the dependence of k_q^1 and k_q^3 on the free energy change, ΔG^{CT}, with (A) acetonitrile, (B) benzene, and with (C) cyclohexane as solvents. Open circles represent k_q^3, and open squares represent k_q^1. The lines passing through experimental points were obtained using eqs 16 and 17 and the parameters listed in Table 4 (see text).

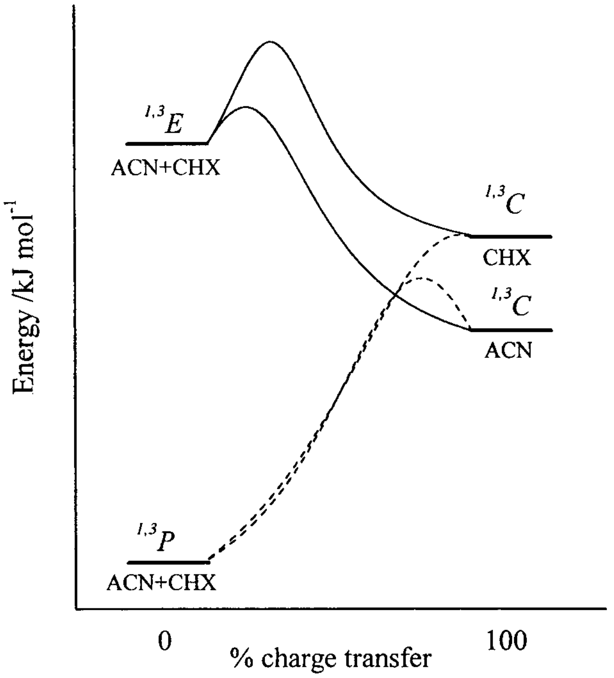

Figure 8. Schematic energy level diagram showing possible minimum energy pathways in acetonitrile (ACN) and cyclohexane (CHX) from ^{1,3}E to ^{1,3}C and from ^{1,3}C to ^{1,3}P labeled $^{1,3}k_T$ and $^{1,3}k_P$, respectively, in Scheme 3, respectively.

the other two solvents can be attributed to the extra stability of the triplet charge transfer complex, which is favored in highly polar solvents, leading to a small activation barrier for internal conversion from ^{1,3}C to ^{1,3}P (see Figure 8). The value of the rate constants for intersystem crossing between the singlet and triplet charge transfer complexes, namely, k_{ST} and k_{TS}, cannot be found from the fit. In acetonitrile, values of $k_{ST} = k_{TS}$ from 0 to 1 × 10^{11} s^{-1} are found to give good fits. Slightly higher values of $k_{ST} = k_{TS}$ (in the range of 0 to 10^{12} and 0 to 10^{13} s^{-1}) can be used to give good fits in benzene and cyclohexane, respectively. However, the goodness of fit is not improved by including any values for these extra steps and therefore this work does not allow us to decide on their presence or absence. It is worth noting that when the values of k_{ST} and k_{TS} are large enough to allow equilibrium to exist between the singlet and triplet charge transfer states, a good fit to the data is not possible.

Conclusions

1. The efficiency of singlet oxygen production, $f_\Delta{}^T$, and the rate constant for triplet state quenching by oxygen, $k_T^{O_2}$, have been measured for biphenyl and nine of its derivatives in acetonitrile, benzene, and cyclohexane. An inverse correlation between $f_\Delta{}^T$ and $k_T^{O_2}$ was observed, and both were found to be strongly dependent on ΔG^{CT}, the free energy change, which is clear evidence for the participation of charge transfer interactions during the quenching process.

2. Calculations for the solvent dependent diffusion rate constant in the three solvents based on measured diffusion coefficients give $k_d = 4.50 \times 10^{10}$, 3.33×10^{10}, and 2.72×10^{10} dm^3 mol^{-1} s^{-1} in acetonitrile, benzene, and cyclohexane, respectively. The solvent dependence of $k_T^{O_2}/k_d$ on ΔG^{CT} indicates the electrostatic interaction energy (term C in eq 6) can be taken as 0, 3, and 20 kJ mol^{-1} for acetonitrile, benzene, and cyclohexane, respectively. Thus our data suggest that changing from the polar solvent, acetonitrile, to nonpolar cyclohexane increases ΔG^{CT} for each of the biphenyl derivatives studied by 20 kJ mol^{-1} since this adjustment makes the quenching rates observed in cyclohexane for a particular E_M^{OX} equivalent to the quenching rates observed in acetonitrile at the same ΔG^{CT}, explaining the lower $k_T^{O_2}$ and higher $f_\Delta{}^T$ in cyclohexane compared to acetonitrile.

3. This work confirms the importance of charge transfer interactions in determining the efficiency of quenching by oxygen. Variations in the yields of singlet oxygen production are shown to arise because of the increasing importance of quenching via the triplet channel when the charge transfer complex formed as a result of electron transfer from the triplet state to molecular oxygen lies at a lower energy than the triplet state. In nonpolar solvents that do not stabilize charge transfer complexes and for the biphenyl derivatives with high oxidation potentials where the energy of the charge transfer complexes formed with oxygen lie at higher energies than the excited triplet states, the yield of singlet oxygen approaches unity. In polar solvents and when the energy of the charge transfer complexes drops below the excited triplet state, the yield of singlet oxygen is much reduced.

4. Our treatment shows that the free energy of activation $\Delta G^\ddagger$ for charge transfer assisted quenching by oxygen has a linear dependence on the free energy change ΔG^{CT} of the form $\Delta G^\ddagger = \alpha + \beta \Delta G^{CT}$ and β values indicate that the transition state for the reaction involves only a small fractional charge transfer that shows an unusual solvent dependence.

5. It has been found that an alternative pathway, $^1k_\Delta$, is taking place alongside the charge transfer pathway in the singlet channel. These pathways are competitive, and their values are found to be solvent dependent.

6. The proposed Scheme 3 enables the evaluation of the rate constants for different pathways included in this scheme by using a minimum of variables to give a good fit to all the data. It is not possible to confirm the presence or complete absence of intersystem crossing between charge transfer states from these data.

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