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Mechanism of Quenching of Triplet States by Oxygen: Biphenyl Derivatives in Acetonitrile

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The rate constants, $k_T^{O_2}$, for oxygen quenching in acetonitrile of the triplet states of biphenyl and nine of its derivatives and the efficiencies of formation thereby of singlet oxygen, f_Δ^T, have been measured as have the oxidation potentials of these derivatives. The rate constants $k_T^{O_2}$ decrease from 12.6×10^9 to 0.88×10^9 dm^3 mol^{-1} s^{-1} as the oxidation potentials of the biphenyls rise from 1.30 to 2.11 V vs SCE while f_Δ^T varies in the opposite direction rising from 0.31 to 0.84 with increasing oxidation potential. The mechanism of quenching via singlet and triplet complexes is discussed. 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. 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 (about 13.5%) charge-transfer character.

Introduction

Despite the intense research carried out over the past three decades on the mechanism of quenching of electronically excited states by molecular oxygen,[1−18] several aspects remain unclear. It is well-known that singlet oxygen is produced with varying efficiency as a consequence of quenching of both excited singlet and triplet states represented as $^1M^*$ and $^3M^*$, respectively, as depicted in Scheme 1. There have been many symbols used to represent these efficiencies which are the fractions of singlet and triplet states quenched by oxygen which yield singlet oxygen $O_2^*(^1\Delta_g)$. These are defined in Scheme 1[14] as f_Δ^S and f_Δ^T, respectively. It is hoped that those working in this area using various symbols, for example, α and ϵ,[19] δ and S_Δ [see, for example, ref 20], α_S and α_T,[15] and even (*a*.*d*) and *b*,[21] will agree to use the same symbols for f_Δ^S and f_Δ^T, respectively, in the future.

The lowest excited singlet states of molecular oxygen are the $O_2^*(^1\Delta_g)$ and the $O_2^*(^1\Sigma_g^+)$ states, which lie 94 and 157 kJ mol^{-1}, respectively, above the $O_2(^3\Sigma_g^-)$ ground state. For triplet sensitizers with energies in excess of 157 kJ mol^{-1}, both the $O_2^*(^1\Sigma_g^+)$ and the $O_2^*(^1\Delta_g)$ state may be formed as a result of quenching by oxygen. In fact recently, Bodesheim et al.[22] have measured the relative efficiencies of production of $O_2^*(^1\Delta_g)$ and $O_2^*(^1\Sigma_g^+)$ for a variety of sensitizers in carbon tetrachloride, a solvent where exceptional emission from $O_2^*(^1\Sigma_g^+)$ can be detected. The proportion of $O_2^*(^1\Sigma_g^+)$ and $O_2^*(^1\Delta_g)$ produced was shown to depend on the energy of the triplet state being quenched, for example, in the case of the triplet state of 9-bromoanthracene in carbon tetrachloride the relative yields of $O_2^*(^1\Sigma_g^+)$ and $O_2^*(^1\Delta_g)$ produced are 42% and 48%, respectively, with the final 10% of quenching collisions yielding the ground state of the oxygen molecule directly.[22] Even in carbon tetrachloride the lifetime of $O_2^*(^1\Sigma_g^+)$ is very short (130 ns), and by detecting the emission from both $O_2^*(^1\Delta_g)$ and $O_2^*(^1\Sigma_g^+)$, Schmidt and Bodesheim[23] were able to show that in carbon tetrachloride $O_2^*(^1\Sigma_g^+)$ decays to give $O_2^*(^1\Delta_g)$ with unit efficiency. In acetonitrile, the solvent used in this work, all indications are that any $O_2^*(^1\Sigma_g^+)$ formed will decay very rapidly to give $O_2^*(^1\Delta_g)$. In Scheme 1 therefore we have used $^1O_2^*$ to represent $O_2^*(^1\Delta_g)$ only, and it is this species that is detected in the experiments reported here. Any $O_2^*(^1\Sigma_g^+)$ formed which did not decay to give $O_2^*(^1\Delta_g)$ would be incorporated in Scheme 1 into step 9, with those included in step 8 representing the production of $O_2^*(^1\Delta_g)$ from oxygen quenching of the triplet state by any route.

Recently we have published a compilation of the quantum yields for the photosensitized formation of the lowest electronically excited state of molecular oxygen in solution,[14] in which we report the quantum yields of singlet oxygen production of 755 different compounds in a wide range of solvents. Despite all these data the reasons certain compounds yield singlet oxygen with high efficiency and others with low efficiency is far from obvious. Most of the studies reported in the compilation[14] have measured the yields of singlet oxygen which results from quenching by oxygen of the triplet states of the compounds concerned, but values of f_Δ^T have been reported only for a small percentage of the compounds studied and measurements of f_Δ^S and $f_T^{O_2}$, the fraction of excited singlet states quenched by oxygen which yield singlet oxygen and which yield triplet states, respectively (see Scheme 1), are rare. 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 $E^M{}_{OX}$ for naphthalene derivatives.[24] Furthermore the values of $k_T^{O_2}$ are higher and the values of f_Δ^T lower for naphthalene derivatives in more

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SCHEME 1

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

$$\left.\begin{array}{ll} 1. & {}^1M^* \xrightarrow{k_F} {}^1M + h\nu_F \\ 2. & {}^1M^* \xrightarrow{k_{ic}} {}^1M \\ 3. & {}^1M^* \xrightarrow{k_{isc}} {}^3M^* \end{array}\right\} k_{SD} = k_F + k_{ic} + k_{isc} \qquad \begin{array}{l} \phi_F^O = k_F/k_{SD} \\ \phi_T^O = k_{isc}/k_{SD} \end{array}$$

$$\left.\begin{array}{ll} 4. & {}^1M^* + {}^3O_2 \xrightarrow{k_{S\Delta}} {}^3M^* + {}^1O_2^* \\ 5. & {}^1M^* + {}^3O_2 \xrightarrow{k_{ST}} {}^3M^* + {}^3O_2 \\ 6. & {}^1M^* + {}^3O_2 \xrightarrow{k_{SO}} \text{Quenching} \end{array}\right\} k_S^{O_2} = k_{S\Delta} + k_{ST} + k_{SO}, \qquad \begin{array}{l} f_\Delta^S = k_{S\Delta}/k_S^{O_2} \\ f_T^{O_2} = \left(k_{S\Delta} + k_{ST}\right)/k_S^{O_2} \\ \phi_F^o/\phi_F = F^o/F = 1 + k_S^{O_2}[O_2]/k_{SD} \end{array}$$

$$P_S^{O_2} = k_S^{O_2}[O_2]/(k_{SD} + k_S^{O_2}[O_2]) = \left(F^o - F\right)/F^o$$

$$\begin{array}{ll} 7. & {}^3M^* \xrightarrow{k_{TD}} {}^1M \end{array}$$

$$\left.\begin{array}{ll} 8. & {}^3M^* + {}^3O_2 \xrightarrow{k_{T\Delta}} {}^1M^* + {}^1O_2^* \\ 9. & {}^3M^* + {}^3O_2 \xrightarrow{k_{TO}} \text{Quenching} \end{array}\right\} k_T^{O_2} = k_{T\Delta} + k_{TO} \qquad \begin{array}{l} f_\Delta^T = k_{T\Delta}/k_T^{O_2} \\ P_T^{O_2} = k_T^{O_2}[O_2]/(k_{TD} + k_T^{O_2}[O_2]) \end{array}$$

$$\left.\begin{array}{ll} 10. & {}^1O_2^* \xrightarrow{k_{\Delta d}} {}^3O_2 \\ 11. & {}^1O_2^* \xrightarrow{k_{\Delta p}} {}^3O_2 + h\nu_p \end{array}\right\} k_\Delta = k_{\Delta p} + k_{\Delta d}$$

polar or polarizable 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.[25] 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 with the exception of 9-methoxyanthracene in acetonitrile, where the value drops to one-third.[25]

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.

Experimental Section

Benzophenone (Aldrich, Gold Label), naphthalene (Aldrich, scintillation grade, Gold Label), 4,4′-dimethoxybiphenyl (Aldrich), 4-methylbiphenyl (Aldrich), 4-chlorobiphenyl (Lancaster, 99%), 4-methoxyacetophenone (Aldrich), and tetrabutylammonium perchlorate TBAP (Fluka, >99%) were used as received. 4-Methoxybiphenyl (Aldrich 97%), 4,4′-dimethylbiphenyl (Aldrich), biphenyl (Aldrich), 4-bromobiphenyl (Aldrich), 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 (Aldrich) was recrystallized from methanol.

For singlet oxygen luminescence measurements, the third harmonic of a Lumonics Q-switched Nd:YAG laser (HY200, 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 f_Δ^T 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_0 at $t = 0$. A typical trace is shown in Figure 1. The luminescence intensity I_0 at zero time was plotted against the laser intensity which was varied using at least 15 points to ensure the plots were indeed linear. The slopes obtained for these straight line plots were compared with those obtained from optically matched standards in the same solvent, thereby yielding relative f_Δ^T values. The absorbances of the optically matched solutions were about 0.5 at 355 nm. A typical set of results is shown in Figure 2.

The same laser was used as the excitation source for kinetic absorption measurements with a 300 W xenon arc lamp as the analyzing source. Full details of the laser flash photolysis instrument used have been given previously.[26] 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 oxygen. The pseudo-first-order decay constant in air saturated solutions, k_{obs}, is given by

$$k_{obs} = k_{TD} + k_T^{O_2}[O_2]$$

where k_{TD} is the first-order rate constant for decay of the triplet state absorption in the absence of oxygen. $k_T^{O_2}$ was obtained using this equation taking the oxygen concentration in air-saturated acetonitrile as 1.9×10^{-3} mol dm^{-3}.[27]

The half-wave oxidation potentials were measured by cyclic voltammetry using an EG&G Princeton Applied Research Model 273 potentiostat. A three-electrode system was employed

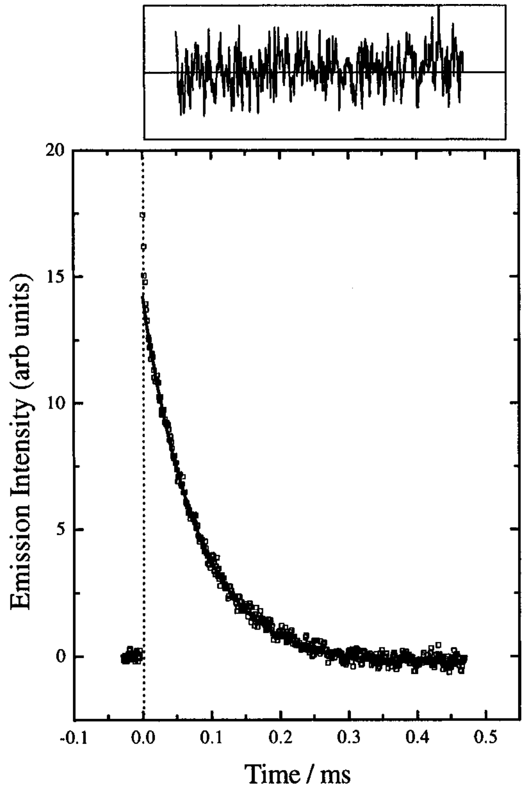


Figure 1. Decay trace due to singlet oxygen phosphorescence following laser excitation of biphenyl in air-saturated acetonitrile. The fitted exponential curve is shown drawn through the experimental points together with a display of the residuals.

with a Pt wire as the working electrode and with a platinum mesh counter electrode. The counter and the reference electrode (SSCE) were each separated from the working electrode compartment of the electrochemical cell by glass frits. The platinum working electrode was pretreated before the investigation of a given compound by immersion in concentrated sulfuric acid. It was then anodized and then cathodized, (2 min each at 100 mA in 0.5 mol dm^{-3} H_2SO_4) followed by washing with deionized water and acetonitrile, before drying with air. Electrode potentials were measured with respect to SSCE at 21 ± 2 °C. The measurements were carried out in deoxygenated acetonitrile solutions containing 10^{-3} mol dm^{-3} of the biphenyl derivative and with 0.1 mol dm^{-3} TBAP as supporting electrolyte. Ferrocene was used as a standard to determine the reliability of the system. The experiments were performed by scanning from 0.00 to + 2.00 V with a scanning speed of 100 mV s^{-1}.

Results and Discussion

Aromatic ketones were used as sensitizers to populate the excited triplet states of the biphenyl derivatives, bypassing their excited singlet states, thus 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,[28] and by Gorman et al.[29] The biphenyl (BP) triplet state is thus populated with unit efficiency by energy transfer from an aromatic ketone (K), viz.

$$^1\mathrm{K}^* \xrightarrow{\phi_T=1} {}^3\mathrm{K}^* \xrightarrow{\mathrm{BP}} {}^3\mathrm{BP}^* \xrightarrow{\mathrm{O_2}} \mathrm{O_2}^*(^1\Delta_g)$$

The quantum yield of singlet oxygen production from the triplet state is given by eq 1 (see Scheme 1):

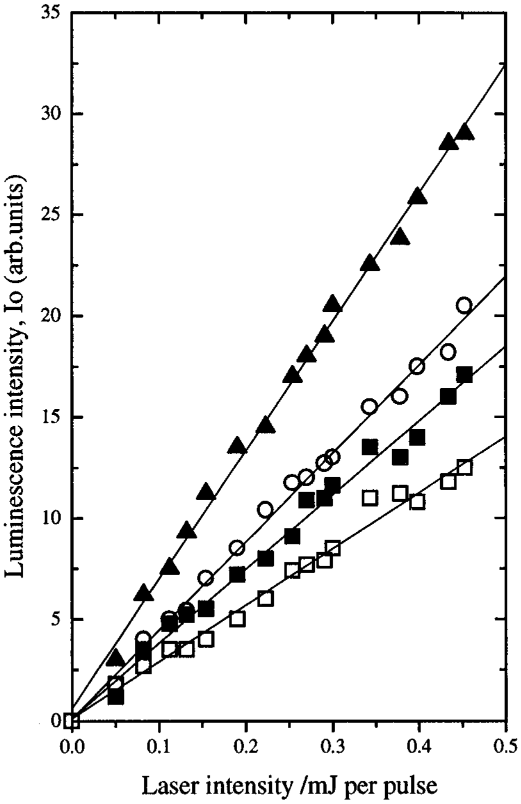


Figure 2. Dependence on laser fluence of the initial luminescence intensity, I_0, due to singlet oxygen phosphorescence following laser excitation of optically matched solutions of benzophenone in acetonitrile containing 4-cyanobiphenyl (▲), 4-chlorobiphenyl (○), biphenyl (■), and 4-methoxybiphenyl (□).

$$\phi_\Delta = \phi_T P_T^{O_2} f_\Delta^T \qquad (1)$$

where ϕ_T is the quantum yield of triplet state production of the biphenyl derivative under the experimental conditions and $P_T^{O_2}$ is the fraction of triplet states produced that are quenched by oxygen. Since the method we employed results in $\phi_T = 1$, it follows that under these conditions

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

For some of the compounds studied here, it was found that the triplet lifetime in the absence of oxygen is relatively short, and therefore we have measured $P_T^{O_2}$ as defined in Scheme 1. In the case of 4,4′-dichlorobiphenyl $P_T^{O_2}$ was 0.75; however, in all other cases $P_T^{O_2}$ was shown to be >0.97. Hence values of f_Δ^T were calculated using eq 2, and these are listed in Table 1 together with values for $k_T^{O_2}$.

For ϕ_Δ measurements we have used two different standards, the first benzophenone/naphthalene in acetonitrile using a value of $\phi_\Delta = f_\Delta^T = 0.62$.[14,24] This standard depends on energy transfer, and the solution has a refractive index that closely matches those of the other measured solutions. The second standard used was acridine in acetonitrile which can be directly excited at 355 nm and has a ϕ_Δ value of 0.82.[30] We have found that the f_Δ^T values measured relative to the two standards are the same within experimental error (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.

The triplet state energy E_T of benzophenone which was used as the ketone sensitizer is 289 kJ mol^{-1} (ref 31), and since this is ~15 kJ mol^{-1} higher than that of the highest triplet state of

TABLE 1: Rate Constants $k_T^{O_2}$ and Singlet Oxygen Formation Efficiencies, f_Δ^T for Oxygen Quenching of the Triplet States of Biphenyl Derivatives in Acetonitrile and Their Half-Wave Oxidation Potentials E_M^{OX} (Estimated Errors ± 10%)

compound	$k_T^{O_2}/10^9$ M^{-1} s^{-1}	f_Δ^T	E_M^{OX}/V vs SCE	$\Delta G^{CT\,a}$/kJ mol^{-1}	$k^1_q(k^1_q\text{cal}^b)/10^9$ M^{-1} s^{-1}	$k^3_q(k^3_q\text{cal}^b)/10^9$ M^{-1} s^{-1}	p_1	p_3
4,4′-dimethoxybiphenyl	12.60	0.31	1.30	−63.3	3.9 (3.8)	8.7 (9.1)	0.95	0.70
4-methoxybiphenyl	8.56	0.36	1.53	−42.1	3.1 (3.2)	5.5 (5.6)	0.75	0.44
4,4′-dimethylbiphenyl	5.93	0.42	1.69	−30.7	2.5 (2.4)	3.4 (3.2)	0.61	0.28
4-methylbiphenyl	4.36	0.44	1.80	−16.1	1.9 (1.9)	2.4 (2.0)	0.47	0.20
biphenyl	2.85	0.48	1.91	−14.5	1.4 (1.4)	1.5 (1.2)	0.33	0.12
4-chlorobiphenyl	2.10	0.56	1.96	−1.6	1.3 (1.2)	0.92 (0.94)	0.29	0.07
4-bromobiphenyl	2.05	0.59	1.95	−1.6	1.2 (1.2)	0.84 (1.0)	0.29	0.07
4,4′-dichlorobiphenyl	1.77	0.58	2.02	7.2	1.0 (1.0)	0.74 (0.64)	0.25	0.06
4,4′-dibromobiphenyl	1.46	0.67	2.01	6.2	0.98 (1.0)	0.48 (0.69)	0.24	0.04
4-cyanobiphenyl	0.88	0.84	2.11[c]	13.8	0.74 (0.75)	0.14 (0.14)	0.18	0.01

[a] Calculated from eq 5; see text. [b] Calculated using eqs 15 and 16 and the values for the constants in Scheme 3 given in the text. [c] From ref 35.

the biphenyls studied here, namely 274 kJ mol^{-1} for biphenyl itself, efficient energy transfer ensues.[32,33] We have confirmed that biphenyl quenching of triplet benzophenone is 100% by measuring the efficiency of sensitized singlet oxygen production from the triplet state of biphenyl (f_Δ^T) using solutions containing constant concentration of benzophenone and different concentrations of biphenyl, extended from 6.4 × 10^{-3} up to 8.8 × 10^{-2} mol dm^{-3}. The singlet oxygen luminescent intensities at time zero I_0 were plotted against the laser intensity; the slopes obtained for these solutions containing biphenyl at these different, but relatively high concentrations, were identical.

Previously[24] 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 triplet 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-methoxyacetophenone, 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.

The half-wave oxidation potentials, E_M^{OX}, that we measured versus SSCE were consistently 0.05 V higher than those measured versus SCE by others.[34] Therefore, to report the half-wave oxidation potentials in terms of SCE rather than SSCE in Table 1, 0.05 V was subtracted from the values measured versus SSCE. In the case of 4-cyanobiphenyl, it was found that the oxidation potential is larger than 2 V, which made the evaluation of the half-wave oxidation potential impossible under our experimental conditions. However, the oxidation potential of 4-cyanobiphenyl and four other monosubstituted biphenyls have been measured[35] versus Ag/AgClO$_4$ using a Pt electrode and tetraethylammonium perchlorate (0.1 M) as a supporting electrolyte in acetonitrile by Tamai et al.[35] The correlation between the half wave oxidation potentials measured by us versus SCE and those measured versus Ag/AgClO$_4$ enables us to evaluate that of 4-cyanobiphenyl by subtracting 0.41 V from the value reported Tamai et al.[35] which was the difference observed for three out of the four compounds measured both by Tamai et al.[35] and by ourselves. This value is also given in Table 1.

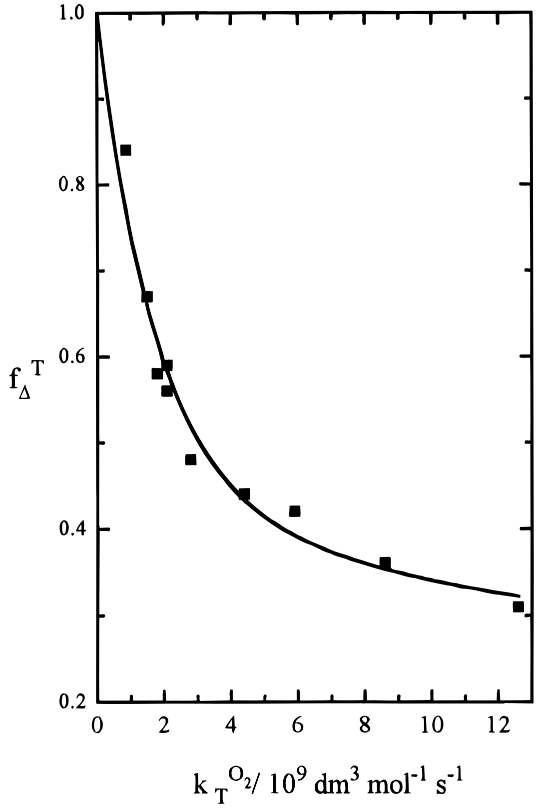


Figure 3. Dependence of f_Δ^T the efficiency of singlet oxygen $O_2^*(^1\Delta_g)$ production during oxygen quenching of triplet states of biphenyl derivatives in acetonitrile on the quenching rate constants $k_T^{O_2}$.

It is clear from Table 1 and Figure 3 that an inverse correlation exists between f_Δ^T and $k_T^{O_2}$. This can be explained simply using Scheme 2.

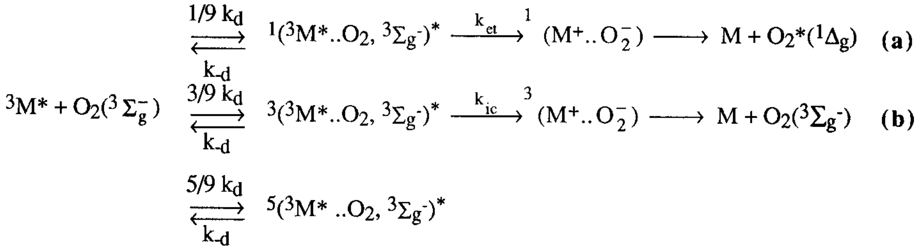
According to Scheme 2

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

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

Thus when more quenching occurs via the triplet channel (b) which does not produce singlet oxygen, the higher value of $k_T^{O_2}$ leads to a lower value of f_Δ^T. Gijzeman et al.[17,18] found that for aromatic hydrocarbons with relatively low triplet state

SCHEME 2



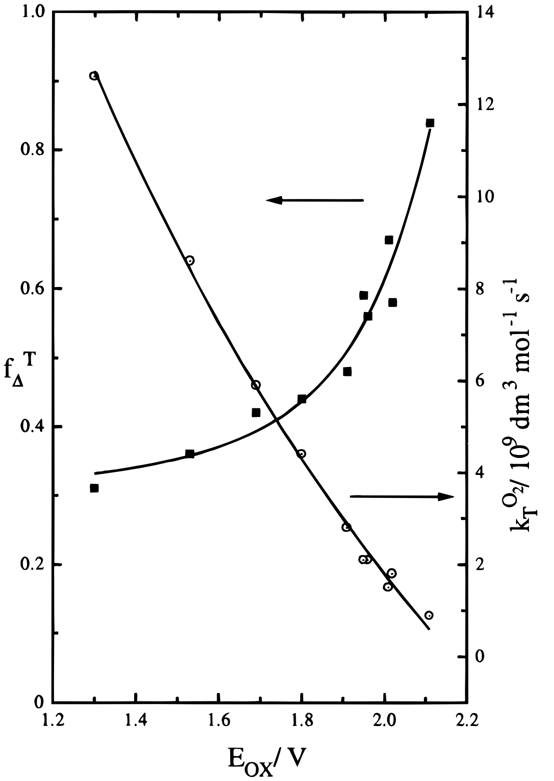


Figure 4. Dependence of f_Δ^T, the efficiency of singlet oxygen formation during oxygen quenching of triplet states of biphenyl derivatives, and the quenching rate constant $k_T^{O_2}$ on the measured half-wave oxidation potential E^{ox}.

energies ($E_T < 200$ kJ mol^{-1}) the observed oxygen quenching rate constants ($k_T^{O_2}$) in benzene, hexane, and cyclohexane were approximately equal to $k_d/9$, implying exclusive quenching via the energy-transfer channel to produce $O_2^*(^1\Delta_g)$ (cf. eq 3 with $k_{et} \gg k_{-d}$ and $k_{ic} \ll k_{-d}$). This was 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.[16] However, much higher oxygen quenching rate constants have been reported by Bent and Schulte-Frohlinde[36] for the triplet states of some stilbene derivatives with values up to 7 × 10^9 dm^3 mol^{-1} s^{-1}, by ourselves[16] for some triplet states in benzene with rate constants up to 14 × 10^9 dm^3 mol^{-1} s^{-1} for the triplet state of *N*-methylindole, by Chattopadhyay et al.[37] for the triplet states of some ketones in acetonitrile and benzene with values of up to 11.4 × 10^9 and 12.6 × 10^9 dm^3 mol^{-1} s^{-1} for triplet *p,p'*-bis(*N,N*-dimethylamino)benzophenone in these two solvents, respectively. More recently we ourselves[24] have reported $k_T^{O_2}$ in excess of $k_d/9$, for a series of naphthalene derivatives in acetonitrile, benzene, and cyclohexane, in this case the maximum value observed was 7.2 × 10^9 dm^3 mol^{-1} s^{-1} for 1-methoxynaphthalene in acetonitrile.

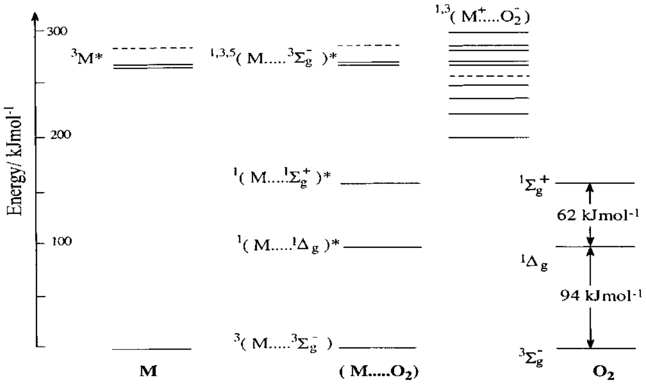


Figure 5. Schematic electronic energy level diagram for substituted biphenyl derivatives (M), molecular oxygen and the complex (M••O$_2$). The energy of the triplet state ^{3}M*, ^{1,3,5}(M••$^3\Sigma_g^-$)*, and ^{1,3}(M$^+$••O$_2^-$) for biphenyl itself are shown as dash lines. Solid lines are given for the other nine derivatives, which have very similar energies for ^{3}M* (between the two lines shown) but show considerable variation in the energy of the charge transfer states ^{1,3}(M$^+$••O$_2^-$) as shown.

Varying the electron-donating nature of the substituent on the biphenyl ring changes E_M^{OX} substantially. The smooth dependence of $k_T^{O_2}$ and f_Δ^T on E_M^{OX}, shown in Figure 4, demonstrates the importance of charge-transfer interactions in determining $k_T^{O_2}$ and f_Δ^T. As shown by Rehm and Weller[38] and by ourselves,[39] a good estimate for the free energy change (ΔG^{CT}) to form ion pairs from neutral molecules in acetonitrile is given by eq 5:

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

where F is the Faraday constant and $E_{O_2}^{red}$ is the half-wave reduction potential for O$_2$ ($^3\Sigma_g^-$) taken to be -0.78 V versus SCE.[40] C is the electrostatic interaction energy, which is inversely proportional to the static relative permittivity, ϵ, of the solvent. Since for acetonitrile $\epsilon = 37$, the term C is likely to be negligible in this case. The energy of the charge transfer states for the complexes of oxygen and the biphenyl derivatives calculated from eq 5 have been used to construct the schematic electronic energy level diagram shown in Figure 5. 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 4 but with slightly more scatter, which suggests that the literature values used for E_T for the biphenyl derivatives are subject to some uncertainty. For compounds with high E_M^{OX} (and hence where ΔG^{CT} is positive), f_Δ^T approaches but does not reach the highest expected value of unity, e.g., $f_\Delta^T = 0.84$ in the case of 4-cyanobiphenyl. This value may be less than unity due to state mixing imparting substantial charge-transfer character into the low-lying M•••O$_2$ states even when $E_{CT} > E_T$, i.e., when ΔG^{CT} is positive.[16,41] When ΔG^{CT} is negative, f_Δ^T drops to 0.31 in the case of 4,4'-dimethoxybiphenyl. Despite the large negative free energy value for electron transfer, no radical ion formation was detected under our experimental conditions. This is a significant finding since we can easily detect the biphenyl radical cation in acetonitrile solution following photoinduced electron transfer to 9,10-dicyanoanthracene as described in ref 42. Our present work confirms that no ion separation occurs during oxygen quenching in acetonitrile of triplet biphenyl derivatives despite the strong evidence illustrated by Figure 4 for the importance of charge transfer interactions.

Rate constants for oxygen quenching as shown in Scheme 2, via pathway (a) which results in energy transfer to oxygen and via pathway (b) which does not, can be calculated from eqs 6 and 7:

$$k_q{}^1 = f_\Delta^T k_T^{O_2} \tag{6}$$

$$k_q{}^3 = (1 - f_\Delta^T) k_T^{O_2} \tag{7}$$

where $k_q{}^1$ and $k_q{}^3$ are the net rate constants for oxygen quenching via the singlet pathway which produces $O_2^*(^1\Delta_g)$ and for the triplet pathway which does not produce $O_2^*(^1\Delta_g)$, respectively. It is clear from Table 1 that $k_q{}^1$ is greater than $k_q{}^3$ when ΔG^{CT} is positive but $k_q{}^3 > k_q{}^1$ as ΔG^{CT} reaches more negative values.

We first suggested in 1977[16] 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 several aromatic molecules.[41,43,44] The diffusion-controlled rate constant for oxygen quenching in acetonitrile can be taken as 3.7×10^{10} dm^3 mol^{-1} s^{-1}.[10] To interpret the results in Table 1, it is interesting first to calculate the limiting values, which can be obtained according to Scheme 2. The efficiency of singlet oxygen generation from the triplet state would be 100% if only quenching via pathway (a) were involved and 25% if pathways (a) and (b) were both diffusion controlled. Thus if the oxygen quenching rate constant is $\leq k_d/9$ ($\sim 4.1 \times 10^9$ dm^3 mol^{-1} 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 $= {}^4/_9 k_d$ ($\sim 16.4 \times 10^9$ dm^3 mol^{-1} 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 ≥ 1.8 V versus SCE, the quenching rate constants are less than 3×10^9 dm^3 mol^{-1} s^{-1} (i.e., $< {}^1/_9 k_d$) but the observed f_Δ^T values lie in the range 0.48–0.84 which is far from unity. This behavior could be attributed to pathway (b) in Scheme 2 being important even when $k_T^{O_2}$ is $< {}^1/_9 k_d$.

It is possible to define the probability of quenching via singlet and triplet channels, p_1 and p_3, respectively, according to Scheme 2, see also ref 44, as

$$p_1 = k_{et}/(k_{-d} + k_{et}) = 9k_q{}^1/k_d \tag{8}$$

and

$$p_3 = k_{ic}/(k_{-d} + k_{ic}) = 3k_q{}^3/k_d \tag{9}$$

then

$$p_1/(1 - p_1) = k_{et}/k_{-d} \tag{10}$$

and

$$p_3/(1 - p_3) = k_{ic}/k_{-d} \tag{11}$$

Values of p_1 and p_3 calculated from eqs 6–9, taking k_d the diffusion-controlled rate constant for oxygen quenching in acetonitrile as 3.7×10^{10} dm^3 mol^{-1} s^{-1},[43] are given in Table 1. When $\log\{p_1/(1 - p_1)\}$ and $\log\{p_3/(1 - p_3)\}$, which from eqs 10 and 11 are equivalent to $\log(k_{et}/k_{-d})$ and $\log(k_{ic}/k_{-d})$, are plotted against ΔG^{CT}, parallel linear plots are observed; see Figure 6. For both plots a slope equal to -0.024 mol kJ^{-1} is obtained in contrast to a slope of -0.178 mol kJ^{-1} expected for quenching due to complete electron transfer, implying that quenching is via complexes with only partial charge transfer.[45]

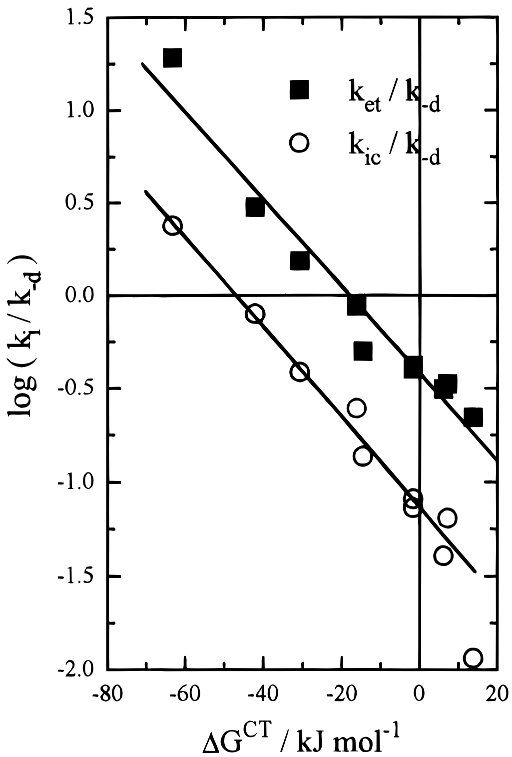
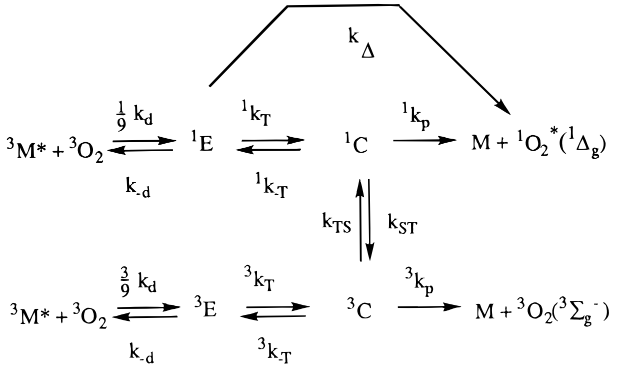


Figure 6. Plots of the dependence of $\log(k_{et}/k_{-d})$ (■) and $\log(k_{ic}/k_{-d})$ (○), on ΔG^{CT}, the free energy change for charge transfer from the triplet state, as calculated from eq 5; see text.

Previously Grewer and Brauer[44] have obtained linear regression plots of the type shown in Figure 6 based on the values they obtained for $k_T^{O_2}$ and f_Δ^T for some ketones and various aromatic hydrocarbons in toluene together with our published values for naphthalene and its derivatives in benzene. They found different slopes of -0.005 and -0.016 mol kJ^{-1} for the singlet and triplet channels, respectively. We have examined our results for naphthalene and several of its derivatives in acetonitrile[25] and obtained linear regression slopes of -0.010 and -0.019 mol kJ^{-1} for singlet and triplet channels, respectively. However, these data show considerably more scatter than that shown in Figure 6 due, we feel, to uncertainties in the literature values of E_M^{OX} which include measurements from different laboratories. Also our naphthalene data[25] shows evidence in agreement with the conclusions of Grewer and Brauer that the singlet channel contains competing energy transfer without charge transfer for results where charge transfer is endoergic or only slightly exoergic.

The parallel plots shown, in Figure 6, could be due to efficient intersystem crossing between singlet and triplet charge-transfer complexes, as has been proposed by ourselves[16] and others,[41,43,44] as shown in Scheme 3, where for simplicity ^{1,3}E and ^{1,3}C, are used to represent the encounter and charge transfer complexes, respectively. Obviously Scheme 3 incorporates Scheme 2 and includes the possibility mentioned above of the direct production of $O_2^*(^1\Delta_g)$ without passing through the charge-transfer complex ^{1}C, i.e., Schemes 2 and 3 are identical when k_Δ, k_{ST}, and k_{TS} are negligibly small.

SCHEME 3



If decay constants for the encounter and the charge-transfer complexes are defined as

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

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

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

$$k_q{}^1 = k_d\{(^1k_T{}^1k_P + {}^1k_Ck_\Delta)(3k_E{}^3k_C - 3k_T3k_{-T}) + 3^3k_Tk_{TS}(^1k_E{}^1k_P + k_{TS}k_\Delta) - {}^3k_Ek_{ST}k_{TS}k_\Delta)\}/9D \quad (12)$$

and

$$k_q{}^3 = k_d{}^3k_P\{3^3k_T(^1k_E{}^1k_C - {}^1k_T{}^1k_{-T}) + {}^3k_E{}^1k_Tk_{ST}\}/9D \quad (13)$$

where

$$D = (^1k_E{}^1k_C - {}^1k_T{}^1k_{-T})(^3k_E{}^3k_C - {}^3k_T{}^3k_{-T}) - {}^1k_E{}^3k_E\,k_{ST}k_{TS} \quad (14)$$

Equations 12 and 13 simplify when k_{ST} and $k_{TS} = 0$ to give

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

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

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

We have attempted to fit the experimental data for $k_q{}^1$ and $k_q{}^3$ using either eqs 12 and 13 or 15 and 16. The fits obtained with eqs 12 and 13 were hardly any better than those obtained using eqs 15 and 16 and therefore the calculated values given in Table 1 alongside the experimental values were for best fits to eqs 15 and 16 using the following parameters: $k_d = 3.7 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, $k_{-d} = 3.7 \times 10^{10}$ s^{-1}, $^1k_p = 10^{14}$ s^{-1}, $^3k_p = 1.4 \times 10^{11}$ s^{-1}, $k_\Delta = 3 \times 10^9$ s^{-1}, $^1k_T = {}^3k_T = 6 \times 10^{12} \exp(-\Delta G^\ddagger/RT)$, $^1k_{-T} = {}^3k_{-T} = 6 \times 10^{12} \exp(-(\Delta G^{CT} - \Delta G^\ddagger)/RT)$.

To get a reasonable fit, it was necessary to use linear and not nonlinear free energy relationships between the free energy for activation for oxygen quenching, $\Delta G^\ddagger$, and ΔG^{CT}, as expected from the data presented in Figure 6. Thus, we took $\Delta G^\ddagger = \alpha\Delta G^{CT} + \beta$, and the best fit was obtained taking $\Delta G^\ddagger = (15.3 + 0.135\Delta G^{CT})$ kJ mol^{-1} within expressions for calculating ^1k_T and $^1k_{-T}$ and $\Delta G^\ddagger = (18.6 + 0.135\Delta G^{CT})$ kJ mol^{-1} in the expressions for calculating ^3k_T and $^3k_{-T}$. Thus, when we assumed k_{ST} and $k_{TS} = 0$, we found the best fits required that the triplet encounter complex had to overcome a free energy of activation to reach the triplet charge-transfer complex higher by 3.3 kJ mol^{-1} than that required to reach the corresponding singlet charge-transfer complex. This could indicate the triplet encounter complex is 3.3 kJ mol^{-1} more stable than the singlet encounter complex (RT ln 3 equals 2.7 kJ mol^{-1}). However, it has to be borne in mind that equally good fits could be obtained if efficient intersystem crosing between singlet and triplet pathways was assumed e.g., taking $\Delta G^\ddagger = (18.1 + 0.135\Delta G^{CT})$ kJ mol^{-1} within all the expressions for calculating ^1k_T, $^1k_{-T}$, ^3k_T, and $^3k_{-T}$ and using $k_{ST} = k_{TS} = 2 \times 10^{10}$ s^{-1}. It is important to note that reasonable fits to the experimental data could not be obtained using values of $\Delta G^\ddagger$ calculated from nonlinear relationships such as the expressions derived by Rehm and Weller,[37] Marcus,[46] or Agmon and Levine.[47] Unfortunately, it is not possible on the basis of these data to prove the presence or absence of intersystem crossings between the singlet and triplet $M{\cdot\cdot}O_2$ charge-transfer complexes. However these results do support as the mechanism for oxygen quenching the involvement of an exciplex mechanism similar to that recently proposed by Kuzmin.[48]

Conclusions

The dependence of the rate constants for oxygen quenching of the triplet states of biphenyl and nine of its derivatives in acetonitrile—and for the efficiency of formation thereby of singlet oxygen—on the measured oxidation potentials clearly demonstrates that charge-transfer-assisted quenching occurs via both singlet and triplet complexes which have only partial (about 13.5%) charge-transfer character.

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