Charge Transfer Interactions in the Generation of Singlet Oxygen $O_2(^1\Delta_g)$ by Strong Electron Donors

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The quenching rate constant of the triplet state by molecular oxygen and the efficiency of singlet oxygen generation have been measured for 12 amines in cyclohexane and benzene. For the best electron donors, the average rate constant for quenching by energy transfer is 6.0×10^9 M^{-1} s^{-1}. For the same compounds, the rate constant of quenching via enchancement of internal conversion is 1.2×10^{10} M^{-1} s^{-1}. The energy transfer component of the total quenching rate constant is almost twice as fast as the maximum from the standard Porter model. The mechanisms of quenching via quintet, singlet, and triplet channels are discussed for amines and aromatic hydrocarbons, and intersystem crossing out of the quintet manifold is proposed.

Introduction

The mechanisms of interaction of the electronically excited states of organic molecules with molecular oxygen have been a classic problem in photochemistry and a field of intensive research for decades.[1−29] It is well-known that the yield of $O_2(^1\Delta_g)$ depends strongly on the sensitizer and solvent nature, but the quenching rate constant of triplets by molecular oxygen is always below the diffusion-controlled limit.[4] Since the pioneering work of Gijzeman, Kaufman, and Porter the quenching of triplet sensitizer has been described within the format given in Scheme 1.[3]

SCHEME 1

$$\underset{k_{\text{-dif}}}{\overset{5/9\,k_{\text{dif}}}{\rightleftharpoons}} {}^5(^3S^{*\cdots}{}^3O_2) \qquad (1)$$

$$^3S^* + {}^3O_2 \underset{k_{\text{-dif}}}{\overset{1/9\,k_{\text{dif}}}{\rightleftharpoons}} {}^1(^3S^{*\cdots}{}^3O_2) \xrightarrow{k_{\text{en}}} S_o + {}^1O_2(^1\Delta_g, {}^1\Sigma_g^+) \qquad (2)$$

$$\underset{k_{\text{-dif}}}{\overset{1/3\,k_{\text{dif}}}{\rightleftharpoons}} {}^3(^3S^{*\cdots}{}^3O_2) \xrightarrow{k_{\text{ic}}} S_o + {}^3O_2 \qquad (3)$$

In this scheme, quenching by energy transfer (eq 2), leading to the production of $O_2(^1\Delta_g)$ and/or $O_2(^1\Sigma_g^+)$, competes with quenching by enhancement of internal conversion (eq 3) with the formation of sensitizer and molecular oxygen in the ground state. Charge transfer interactions have been demonstrated to be responsible for quenching by the triplet pathway (eq 3) and exciplexes have been experimentally implicated.[1−29]

According to Scheme 1, the observed quenching rate constant of the triplet sensitizer by O_2 is given by eq 4 and the probability of singlet oxygen generation by eq 5. This scheme gives an excellent qualitative rationalization for the observed triplet quenching rates and S_Δ (efficiency of singlet oxygen formation) values.

$$^3k_q = \frac{1}{9}k_{\text{dif}}\frac{k_{\text{en}}}{k_{\text{en}} + k_{-\text{dif}}} + \frac{1}{3}k_{\text{dif}}\frac{k_{\text{ic}}}{k_{\text{ic}} + k_{-\text{dif}}} \qquad (4)$$

$$S_\Delta = \frac{1}{9}k_{\text{dif}}\frac{k_{\text{en}}}{k_{\text{en}} + k_{-\text{dif}}}\frac{1}{^3k_q} \qquad (5)$$

Because $O_2(^1\Sigma_g^+)$ has a very short lifetime in liquid solvents and decays to $O_2(^1\Delta_g)$ with quantitative efficiency,[21,24,29] measurement of $O_2(^1\Delta_g)$ yield allows a direct estimate of the efficiency of S_Δ in spite of different relative yields of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ for various sensitizers.

When quenching occurs only via energy transfer, the maximum values should be $^3k_q = (1/9)k_{\text{dif}}$ and $S_\Delta = 1$, according to eqs 4 and 5. This has been observed for substituted anthracenes in cyclohexane.[22] In the case of diffusion-controlled quenching through both pathways 2 and 3, the expected values are $^3k_q = (4/9)k_{\text{dif}}$ and $S_\Delta = 0.25$. However these values are rarely observed. In order to explain such discrepancies, intersystem crossing between singlet and triplet channels in Scheme 1 has been proposed.[6,18,25,28]

It was worthwhile to study $O_2(^1\Delta_g)$ generation by amines and other strong electron donors with highly energetic triplet states because they should be at or near the limit where the limiting values are expected for both the singlet and triplet quenching channels. We report here the quenching rate constants of triplet states of amines by molecular oxygen and the efficiency of $O_2(^1\Delta_g)$ generation in cyclohexane and benzene. Total quenching rate constants are broken up into energy transfer and charge transfer components. We conclude that it is necessary to include intersystem crossing from quintet charge-transfer complexes to account for the experimental data.

Experimental Section

Absorption spectra were recorded on a Shimadzu UV-2101 PC spectrophotometer. Solutions were deaerated by Ar bubbling for 15 min. Experiments were carried out at ambient temperature, 23 °C. Spectro grade solvents were used as received. All other compounds were purchased from Aldrich and purified as necessary by recrystallization or sublimation in a vacuum.

The transient absorption spectra and decay kinetics of triplet sensitizers were studied using nanosecond laser photolysis, as described elsewhere.[30] Solutions were excited in a 1 cm quartz cell by unfocused laser pulses ($\lambda_{\text{ex}} = 266$ or 355 nm, 5 ns, 5

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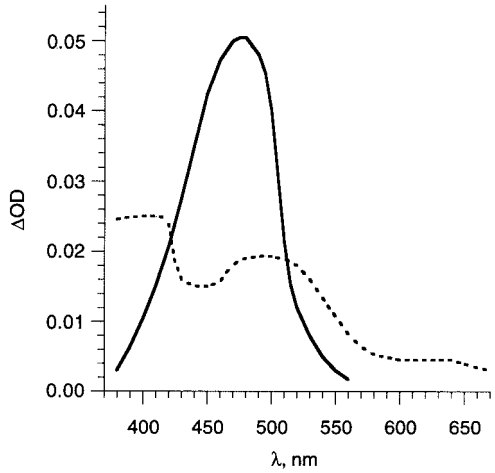


Figure 1. Triplet−triplet absorption spectra of *p*-phenylenediamine in cyclohexane (solid line) and 1-aminonaphthalene in benzene (dotted line).

mJ, 6 mm beam diameter) of a Continuum Surelite Nd:YAG laser. In cyclohexane, 266 nm excitation was used, while 355 nm excitation was used in benzene. Several shots were typically averaged for improved signal to noise. Singlet oxygen luminescence was recorded at 1.27 μm at 90° to the excitation beam,[31] and quantum yields were determined by extrapolating the intensities of emission to the center of the laser pulse. Singlet oxygen yields were linear with laser energy. Solutions of perinaphthenone in cyclohexane and benzene were used as a standard with $\Phi_\Delta = 1$.[32]

The decay kinetics of triplet sensitizers were measured at the maximum of their respective triplet−triplet absorption spectra (λ_{max}^{T-T}). Solutions were saturated with air or oxygen at different pressures, taking into account the partial pressure of the solvent, with total pressures measured using a column of mercury. The solubility of oxygen in air-saturated solution was taken to be 1.9 mM and 2.4 mM in benzene and cyclohexane, respectively.[33]

Fluorescence lifetimes were measured with an Edinburgh Instruments FL 900 single photon counting fluorimeter. The quenching rate constants of the amines' singlet and triplet states (^1k_q and ^3k_q) were obtained from linear plots of experimental rate constants of decay of fluorescence and T−T absorption versus O_2 concentration, respectively. Pulsed conductivity experiments were carried out in a 1 cm quartz cell using electrodes separated by 6 mm (600 V, $R_1 = 200\ \Omega$).

Solutions were prepared with optical densities of 0.2−0.3 at the excitation wavelength. In cyclohexane, this corresponded to approximate concentrations of 30 μM for *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), *N,N*-diethylaniline, and diphenylamine; 60 μM for triphenylamine, 100 μM for *N,N*-dimethylaniline, carbazole, and *p*-phenylenediamine; and 300−600 μM for phenothiazine, 1-naphthylamine, *N,N,N′,N′*-tetramethylbenzidine, and aniline.

Results

The triplet−triplet absorption spectra of 1-naphthylamine and *p*-phenylenediamine were unknown and measured in this work. These are shown in Figure 1.

The excitation of amines in cyclohexane and benzene, being nonpolar solvents, leads to population of the triplet state but not to one-photon photoionization. In no case was the radical cation of the amine observed in flash photolysis experiments, nor were ions detected by transient conductivity. Control experiments in methanol showed ions by both methods.

The triplet yields (Φ_T°) of phenothiazine, 3-chlorophenothiazine, 1-naphthylamine, and *p*-phenylenediamine were measured using the method of energy transfer to β-carotene. Anthracene ($\Phi_T^\circ(A) = 0.72$)[1] in the same solvent was used as the standard. Equation 6 was used to determine these values:

$$\Phi_T^\circ = \Phi_T^\circ(A)\frac{\Delta OD}{\Delta OD(A)}\frac{k_{obs}}{k_{obs}-k_o}\frac{k_{obs}(A)-k_o(A)}{k_{obs}(A)} \quad (6)$$

where ΔOD and ΔOD(A) are the T−T absorption of β-carotene at 530 nm using the amine and anthracene as sensitizers, respectively; k_o is the decay rate constant of the sensitizer in deoxygenated solution, and k_{obs} is the same rate constant with β-carotene added. The optical density of the solutions at λ_{ex} and the concentrations of β-carotene were identical in the control and experimental samples. These results are shown in Table 1.

The observed fluorescence lifetimes (τ_{fl}°) agree well with the literature data.[1,33,47] The flash photolysis experiments indicated that the quenching of fluorescence by O_2 is accompanied by an increase in Φ_T. The quantum yield of singlet oxygen production (Φ_Δ) was measured in air- and O_2-saturated solutions and these data are also in Table 1. The efficiency of $O_2(^1\Delta_g)$ generation was estimated using eq 7, where the triplet yield of the triplet sensitizer including the fluorescence quenching portion is given by eq 8. The average value of S_Δ is shown in Table 1.

$$S_\Delta = \Phi_\Delta/\Phi_T \quad (7)$$

$$\Phi_T = \frac{\Phi_T^\circ + {}^1k_q\tau_{fl}^\circ[O_2]}{1 + {}^1k_q\tau_{fl}^\circ[O_2]} \quad (8)$$

For all but one of the amines, the energy gap between the thermalized fluorescent state and the triplet state is less than 8000 cm^{-1}, [1,33,38,47] and thus singlet oxygen production by the enhanced intersystem crossing pathway can be neglected. The exception to this is 1-naphthylamine. Despite this, the efficiency of singlet oxygen generation in the singlet quenching was estimated to be only 0.03.

Aromatic amines are efficient quenchers of singlet oxygen.[48−50] The mechanism is reversible charge transfer, and thus the better electron donors are the faster quenchers. For TMPD, the rate constant is 5.3×10^8 M^{-1} s^{-1} in cyclohexane, and for tetramethylbenzidine, the rate constant is 2.7×10^8 M^{-1} s^{-1} in benzene. Under the conditions used in these experiments, the $O_2(^1\Delta_g)$ lifetime decreased from 20 μs in cyclohexane to 15 μs when TMPD was added, and from 30 μs in benzene to 24 μs with tetramethylbenzidine added. Thus, we are able to determine Φ_Δ values while neglecting this possible complication.

The triplet state of triphenylamine decays to the triplet of *N*-phenyldihydrocarbazole, which has an absorption maximum at 430 nm, with a decay rate constant of 1.8×10^6 s^{-1}.[46] The S_Δ value given in Table 1 was estimated taking into account the value of ^3k_q, the lack of complete triplet quenching of Ph_3N, and $O_2(^1\Delta_g)$ production by triplet *N*-phenyldihydrocarbazole at various oxygen concentrations.

Discussion

In this section, we will analyze data obtained in cyclohexane and in benzene together. Though there are certainly properties about these solvents which differ, their viscosities and dielectric constants are quite similar,[33] as are the rate constants for quenching of excited singlets by O_2.[2,23] Further, to enhance the

TABLE 1: Photophysical Properties of Amines in Cyclohexane and Benzene

compound	τ_o^{fl} (ns)	^1k_q (10^{10} M^{-1} s^{-1})	λ_{max}^{T-T} (nm)	^3k_o (10^5 s^4)	^3k_q (10^{10} M^{-1} s^{-1})	Φ_T^o	Φ_Δ^{air}	$\Phi_\Delta^{O_2}$	S_Δ
p-phenylenediamine	3.3	3.4	475	5.0	2.0	0.5	0.18	0.20	0.28
TMPD	4.2	3.6	620[a]	6.0	2.15	0.96[a]	0.33	0.34	0.34
diethylaniline	2.3	2.7	~450	3.5	1.5	0.9[b]	0.35	0.36	0.38
dimethylaniline	2.6	3.0	460[c]	4.5	1.6	0.9[c]	0.29	0.33	0.34
tetramethylbenzidine[d]	10.3	3.3	475[c]	1.4	1.73	0.52[f]	0.35	0.44	0.47
tetramethylbenzidine[g]	10.7	4.3	475[c]	4.0	2.0	0.52[h]	0.35	0.46	0.50
diphenylamine	2.2	3.1	530[i]	14	1.8	0.32[b]	0.09	0.11	0.20
aniline	4.2	2.8	420[j]	3.0	1.6	0.75[k]	0.15	0.21	0.21
phenothiazine[g]	1.1	3.1[l]	460[m]	2.2	1.7	0.85	0.52	0.54	0.61
3-chlorophenothiazine[g]	0.92		470[m]	1.5	1.6	0.95	0.62	0.65	0.67
carbazole	13.6	2.7	418[n]	0.9	0.83	0.36[o]	0.27	0.40	0.43
triphenylamine	2.2	3.1	520[p]	300	1.5	0.88[o]	0.43	0.63	0.77
1-naphthylamine[g]	8.8	2.9	490	2.0	1.4	0.26	0.25	0.40	0.48

[a] Reference 34. [b] In toluene.[35] [c] Reference 36. [d] λ_{ex} = 355 nm. [e] Reference 37. [f] Reference 38. [g] In benzene. [h] Assumed to be the same as cyclohexane. [i] Reference 39. [j] Reference 40. [k] References 41 and 42. [l] In methanol, ref 33. [m] Reference 43. [n] Reference 44. [o] Reference 45. [p] Reference 46.

TABLE 2: Photophysical Properties of Aromatic Compounds in Cyclohexane and Benzene

sensitizer	^1k_q (10^{10} M^{-1} s^{-1})	^3k_q (10^{10} M^{-1} s^{-1})	S_Δ
naphthalene	2.7[a,b]	2.1[c]	0.62[c]
1-methoxynaphthalene		5.0[c]	0.34[c]
2-methoxynaphthalene		3.5[c]	0.50[c]
1-methylnaphthalene	3.2[a,b]	2.6[c]	0.56[c]
2-methylnaphthalene	2.5[a,b]	2.5[c]	0.57[c]
2-bromonaphthalene		1.5[c]	0.66[c]
1-bromonaphthalene		1.5[c]	0.73[c]
1-cyanonaphthalene		1.2[c]	0.75[c]
1-nitronaphthalene		1.3[c]	0.83[c]
acenaphthene	2.6[a,b]	4.4[c]	0.40[c]
biphenyl	2.8[a,b]	1.4[b]	0.52[d]
fluoranthene[e]	3.9[f]	1.93	0.73
6-aminochrysene[e]		7.68	0.27
9-methylcarbazole[e]	2.5[g]	14.6	0.45
triphenylene[e]	2.0[a,b]	1.6	0.54
phenanthrene	2.3[a,b]	2.0[b]	0.3[h]
chrysene	2.9[a,b]	1.4[b]	0.3[h]
1,3,5-triphenylbenzene		1.1[i]	0.4[h]
1-methylindole		14.0[b]	0.35[j]
Michler's ketone		12.3[k]	0.24[k]
Michler's ketone[a]		11.0[k]	0.32[k]

[a] In cyclohexane. [b] Reference 33. [c] Reference 23. [d] The average of values in ref 4. [e] In toluene.[25] [f] Estimated from the Stern–Volmer constant[52] and fluorescence lifetime.[33] [g] Estimated from the Stern–Volmer constant[25] and fluorescence lifetime.[47] [h] In hexane.[3,10] [i] Reference 3. [j] Reference 4. [k] Reference 53.

discussion of the quenching of triplet states quenching by molecular oxygen, we will use data that are available in the literature for aromatic hydrocarbons that have moderately low oxidation potentials. These data are given in Table 2. Finally, we assume that reencounter kinetics are adequately described by kinetic schemes such as those in Scheme 2, and we do not take take into account any possible small nonequilibrium distributions of reactants.[51]

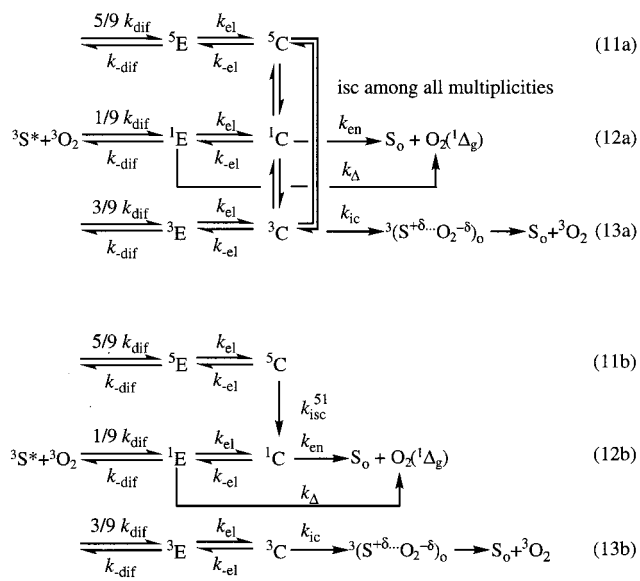
The total triplet quenching rate constant ^3k_q can be broken down into its energy transfer (i.e., $^1O_2$-forming) and charge transfer components. This is accomplished with eqs 9 and 10. These estimates, together with the triplet state energies (E_T) and oxidation potentials, are shown in Table 3.

$$k_q^{en} = S_\Delta \cdot {}^3k_q \tag{9}$$

$$k_q^{CT} = (1 - S_\Delta)\,{}^3k_q \tag{10}$$

To facilitate the analysis done in the remainder of this section, it is useful to define limiting regions of behavior in these rate

SCHEME 2



constants. Somewhat arbitrarily, we take the first eight compounds in Table 3 to represent our region of maximum rate constants. These compounds are also the first data points in Figure 2. They have low oxidation potentials (<1 V vs SCE) and high triplet energies (≥21 800 cm^{-1}). We estimate the experimental diffusion-controlled limit from the average of the ^1k_q values and obtain $k_{dif} = (3.3 \pm 0.4) \times 10^{10}$ M^{-1} s^{-1}, where the error limit is the 95% confidence limit of the mean.

For this same set of eight compounds, the average triplet quenching rate constant components are also figured: $\langle k_q^{en} \rangle = (6.0 \pm 1.4) \times 10^9$ M^{-1} s^{-1} and $\langle k_q^{CT} \rangle = (1.15 \pm 0.16) \times 10^{10}$ M^{-1} s^{-1}. According to Scheme 1, the maximum values for these should be $k_q^{en} = (1/9)k_{dif} = (3.7 \pm 0.4) \times 10^9$ M^{-1} $s^{-1}$and $k_q^{CT} = (1/3)k_{dif} = (1.1 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}. Thus, the experimental quenching rate constant for energy transfer (the singlet channel) is almost twice as large as can be expected according to Scheme 1, whereas the charge transfer component is in line with expectations. Though the standard deviations of the averages are fairly large, the size of the difference suggests that it is real. Moreover, the choice of these eight compounds as the "plateau" is conservative; if the next four are included, for instance, $\langle k_q^{en} \rangle$ actually rises to $(7.2 \pm 1.5) \times 10^9$ M^{-1} s^{-1}. Thus, we conclude that the value of $\langle k_q^{en} \rangle$ is above $(1/9)k_{dif}$ beyond experimental error.

TABLE 3: Triplet Energies, Charge Transfer Properties, and Quenching Rate Constants

sensitizer	E_T[a] (cm^{-1})	$E^{1/2}_{ox}$[b] (V vs SCE in CH_3CN)	ΔG_{et} eV	k_q^{CT} (10^9 M^{-1} s^{-1})	k_q^{en} (10^9 M^{-1} s^{-1})
p-phenylenediamine	25 300[c]	0.24	−1.93	14.4	5.6
TMPD	22 700[d]	0.16[e]	−1.69	14.2	7.3
diethylaniline	27 000	0.76[f]	−1.62	9.3	5.7
dimethylaniline	26 500	0.71	−1.61	10.6	5.4
tetramethylbenzidine	21 800	0.38[r]	−1.35	9.2[g]	8.1[g]
				10.0[h]	10.0[h]
diphenylamine	25 200	0.83	−1.32	14.4	3.6
aniline	24 800	0.87	−1.23	12.6	3.4
1-methylindole	24 200	0.81[i]	−1.22	9.1	4.9
phenothiazine	21 100	0.54[j]	−1.11	6.6	10.4
9-methylcarbazole	24 700[k]	1.1	−1.0	8.0	6.6
triphenylamine	24 300	1.06[f]	−0.98	3.5	11.6
3-chlorophenothiazine	20 600[l]	0.62[j]	−0.97	5.3	10.7
Michler's ketone	23 000	0.95[m]	−0.93	7.5[h]	3.0[h]
				9.4[g]	3.5[g]
carbazole	24 540	1.16	−0.91	4.73	3.6
1-naphthylamine	19 150	0.54	−0.86	7.3	6.7
6-aminochrysene	18 900[k]	0.68[n]	−0.69	5.6	2.1
acenaphthene	20 870	1.21[a]	−0.41	2.64	1.8
triphenylene	23 400	1.55	−0.38	0.74	0.86
1-methoxyhaphthalene	21 000[o]	1.38	−0.25	3.3	1.12
phenanthrene	21 770	1.50	−0.23	1.4	0.60
1-methylnaphthalene	21 200	1.43	−0.23	1.14	1.46
2-methylnaphthalene	21 300	1.45	−0.22	1.08	1.43
2-methoxynaphthalene	21 730[o]	1.52	−0.20	1.75	1.75
chrysene	20 000	1.45	−0.16	0.98	0.42
naphthalene	21 180	1.54	−0.12	0.80	1.3
1,3,5-triphenylbenzene	22 500	1.81[p]	−0.01	0.66	0.44
biphenyl	22 870	1.91[q]	0.04	0.67	0.73
fluoranthene	18 450	1.45	0.13	0.52	1.4
2-bromonaphthalene	21 100	1.90	0.25	0.51	1.0
1-bromonaphthalene	20 650	1.85	0.26	0.41	1.1
1-cyanonaphthalene	20 100	1.95[o]	0.42	0.30	0.90
1-nitronaphthalene	19 300	1.92	0.5	0.22	1.08

[a] Reference 33. [b] Reference 54. [c] Reference 55. [d] Estimated from the O−O band in phosphorescence spectrum in ref 56. [e] Reference 57. [f] Reference 58. [g] In cyclohexane. [h] In benzene. [i] Reference 59. [j] Estimated from the half-wave oxidation potential vs Ag/Ag^+ 0.1 M $AgNO_3$ in ref 43 adding 0.3 V as recommended in ref 54. [k] Reference 25. [l] Reference 60. [m] Reference 61. [n] Estimated from the half-wave oxidation potential vs Ag/Ag^+ 0.1 M $AgNO_3$ in ref 62 adding 0.3 V as recommended in ref 54. [o] Reference 23. [p] Estimated in ref 10. [q] Reference 28. [r] The average value of 0.32 and 0.43 in ref 33.

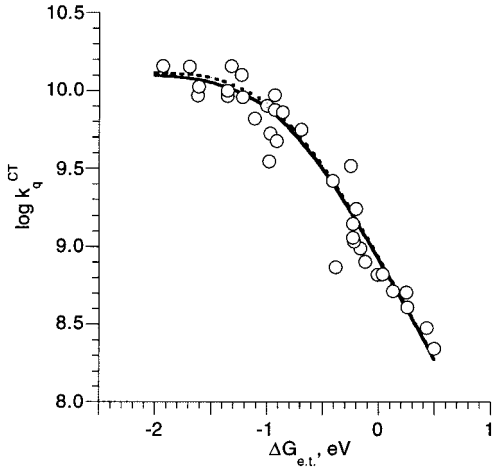


Figure 2. Dependence of the quenching rate constant via charge transfer interactions on the free energy of full electron transfer. The solid line is the Rehm−Weller curve (eq 15) with parameters $A = 10^{12}$ s^{-1}, $\delta = 0.08$, $\lambda = 0.15$ eV, $k_{ic} = 6 \times 10^9$ s^{-1}, and $(1/3)k_{dif} = 1.4 \times 10^{10}$ M^{-1} s^{-1}. The dotted line is with $A = 10^{13}$ s^{-1} and the other parameters given above.

The salient conclusion from these compounds is drawn from the following evidence: (1) the rate constant of energy transfer is greater than can be accounted for without invoking intersystem crossing from channels of other multiplicities into the singlet channel; (2) the rate constant for charge transfer quenching in the triplet channel is at or perhaps slightly above similar expectations; and (3) there exists a pool of quintet collision complexes that account for a majority of the actual collisions. These observations can all be accounted for by invoking intersystem crossing out of the quintet collision and/or charge transfer complexes. Just as it has previously been proposed that triplet−singlet intersystem crossing occurs in these systems, we suggest that the quintet collision and/or charge transfer complexes also undergo intersystem crossing into the triplet and/or singlet manifold.

On the basis of the present data, we cannot distinguish between direct intersystem crossing from the quintet to the singlet manifold, or the more physically reasonable intersystem crossing among all the spin manifolds at various rates that leads to a net transfer of population from the quintet to the singlet manifold. This is illustrated in Scheme 2, adapted from Wilkinson, in which collision complexes and charge transfer complexes ($amine^{\delta+}\cdot O_2^{\delta-}$) have been abbreviated as E and C, respectively. In Scheme 2b is given the simplest scheme that accommodates the data; i.e., it includes an intersystem crossing step from the quintet to the singlet manifold. It also includes a step (k_Δ) that allows for energy transfer in the singlet manifold without formation of a charge transfer complex. Using this simplified scheme, estimation of the net rate of isc out of the quintet manifold remains tractable.

Next, we consider the charge-transfer component of the quenching interaction.[57,63,64] Using the standard Rehm−Weller treatment, the free energy for electron transfer in nonpolar solvent is given by eq 14.

$$\Delta G_{et} = E_{ox}^{1/2}(A/A^{\bullet+}) - E_{red}^{1/2}(O_2/O_2^{\bullet-}) - E_T + \Delta \quad (14)$$

The half-wave oxidation potential of sensitizer vs SCE in acetonitrile is $E_{ox}^{1/2}$ and $E_{red}^{1/2}(O_2/O_2^{\bullet-}) = -0.82$ V.[54] The term Δ compensates for the fact that redox potentials measured in acetonitrile are not the same as in other solvents. Weller et al. have shown that $\Delta = 0.15$ eV for a set of 60 exciplexes in hexane[63] and Wilkinson successfully used this value for the quenching of naphthalenes by oxygen in cyclohexane.[23] We adopt this value for cyclohexane and benzene. The calculated k_q^{CT} values are plotted against $\Delta G_{et,}$ in Figure 2.

The observed quenching rate constant via the charge transfer quenching (process 13b) is described by eq 15. A fit to the data in Figure 2 and estimates of k_{ic} can be obtained if all the other parameters are worked out

$$k_q^{CT} = \frac{{}^1/_3 k_{dif}}{1 + \frac{k_{-dif}}{k_{el}} + \frac{k_{-dif}}{k_{ic}K_{el}}} \quad (15)$$

The equilibrium constant for formation of the charge transfer complex and its forward rate are given by eqs 16 and 17.

$$K_{el} = k_{el}/k_{-el} = \exp(-\Delta G_{ex}/RT) \quad (16)$$

$$k_{el} = A \exp(-\Delta G^{\ddagger}_{ex}/RT) \quad (17)$$

Using the Marcus formulation, the activation energy for electron transfer is given by eq 18.[64] Equation 19 expresses the reorganization energy λ as an internal (λ_i) and solvent component (λ_s).

$$\Delta G^{\ddagger}_{ex} = (\Delta G_{ex} + \lambda)^2/4\lambda \quad (18)$$

$$\lambda = \lambda_i + \lambda_s \quad (19)$$

The free energy for a partial charge transfer in the quenching by O_2 is taken to be given by eq 20.[28,65,66] The fraction δ is taken from the slope of the linear portion of Figure 2 ($\Delta G_{et} > -0.5$ eV) divided by the expectation for full electron transfer, which is $-(2.3RT)^{-1} = -17.0$ eV^{-1}. The present value is $\delta = 0.08$, in line with Wilkinson's value of 0.135 for a series of biphenyl derivatives in acetonitrile.[28]

$$\Delta G_{ex} = \delta \Delta G_{et} \quad (20)$$

The value of k_{-dif} may be estimated from the Eigen−Fuoss equation[67]

$$k_{dif}/k_{-dif} = 4\pi N r^3/3000 \quad (21)$$

where N is Avogadro's number and $r = r_s + r(^1\Delta_g)$, the internuclear distance in a collision complex. Assuming an average value of $r_s = 4$ Å for the sensitizers and a radius of 1.22 Å for $O_2(^1\Delta_g)$,[68] an estimate of $k_{-dif} = 9.2 \times 10^{10}$ s^{-1} is obtained.

Using these estimates and eq 15, an expression to generate k_{ic} can be obtained.

$$k_{ic} = \frac{\exp(\Delta G_{ex}/RT)}{0.12M^{-1}\, k_q^{CT-1} - 1.1 \times 10^{-11}\ \mathrm{s} - A^{-1} \exp(\Delta G^{\ddagger}_{ex}/RT)} \quad (22)$$

In the range of $\Delta G_{et} > -0.5$ eV, the last term in the denominator can be neglected and k_{ic} is approximately 6×10^9 s^{-1}. Analysis of the expression in other regions of the data indicated that physically reasonable values of k_{ic} could only be obtained when A was in the range of $10^{12}-10^{13}$ s^{-1}, a range that itself is physically reasonable.

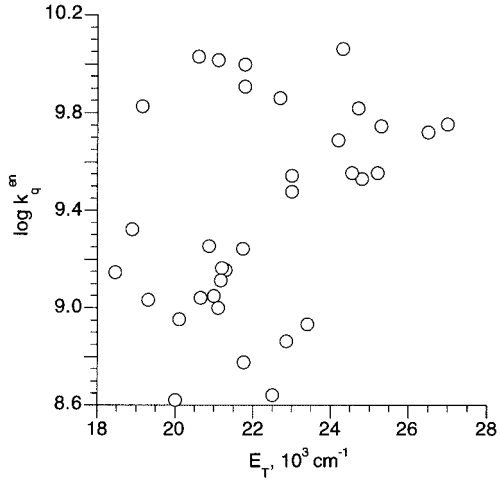


Figure 3. Dependence of the quenching rate constant via energy transfer on the energy of the triplet state of the sensitizer.

The data for k_q^{CT} versus ΔG_{et} are fit to eq 15 and 16 in Figure 2 using λ and A as adjustable parameters. The fit is not very sensitive to the chosen value of A in the range of $10^{12}-10^{13}$, as illustrated. A value of $\lambda = 0.15$ eV was obtained in the best fit. The standard solvent dielectric continuum model equation for solvent reorganization energy suggests that λ_s is very small in nonpolar solvents with low dielectric constants. Thus, the great majority of this energy corresponds to internal reorganization.

It is interesting to note that the datum for Michler's ketone, whose carbonyl-containing structure is different than the others, but whose triplet state is known to contain a strong intramolecular charge transfer character, fits very well in the rest of the data in Figure 2.

Another interesting case is triphenylamine. It is an efficient generator of $^1O_2$ ($S = 0.77$), but its value for k_q^{CT} of 3.5×10^9 M^{-1} s^{-1} is significantly lower than that for other amines with similar values of ΔG_{et}. An appealing interpretation of this is that the energy transfer does not require any particularly demanding conformation, but that the charge-transfer interaction requires a specific interaction between the amine nitrogen and the O_2, which is hindered by the presence of the three phenyl groups. This is an interesting contrast to the charge transfer quenching *of* singlet oxygen *by* amines in acetonitrile, in which no particular steric effect was observed.[50]

There is not any obvious dependence of the experimental k_q^{en} values on the triplet energy of the sensitizer, as illustrated in Figure 3. By contrast, there is at least a qualitative upward trend with decreasing ΔG_{et}, as illustrated in Figure 4. The charge transfer and exchange interactions of molecular oxygen with hydrocarbons leads to an increase of spin−orbital coupling and more efficient mixing of states of different multiplicities.[69−74] From the current data at low ΔG_{et}, we posit that k_q^{en} values over $(1/9)k_{dif}$ are due to net intersystem crossing into the singlet manifold from the quintet exciplex, accompanied by high k_{el} and k_{en}.

Judging by the value of δ, the (amine$^{\delta+}$•$O_2^{\delta-}$) exciplex has a very low degree of charge transfer, and thus the picture of the exciplex as locally excited on the amine is largely representative of its structure. As a result, it can be assumed that the k_Δ process shown in Scheme 2 (energy transfer directly in the encounter complex) occurs, and probably at a rate similar to k_{en}. If the simplified version of Scheme 2 is adopted, and the

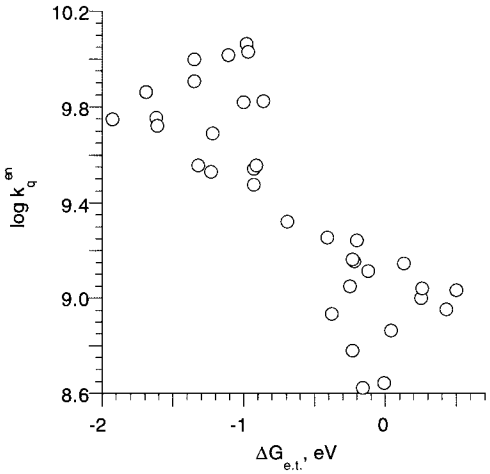


Figure 4. Dependence of the quenching rate constant via energy transfer on the free energy of electron transfer.

assumption is made that $k_\Delta = k_{en}$, a rough estimate of k_{isc}^{51} can be obtained.

Using the steady-state treatment of the intermediates in Scheme 2, eq 23 is found for the rate constant of energy transfer, where the new term α is given by eq 24. There is no explicit dependence on the triplet energy of the sensitizer, but none was observed experimentally (Figure 3).

$$k_q^{en} = \frac{1}{9}k_{dif}\frac{1+\alpha\frac{k_\Delta}{k_{el}}}{1+\alpha\left(\frac{k_\Delta + k_{-dif}}{k_{el}}\right)} + \frac{5}{9}k_{dif}\frac{1+\frac{k_{-dif}}{k_{el}}+\alpha\frac{k_\Delta}{k_{el}}}{\left[1+\alpha\left(\frac{k_\Delta + k_{-dif}}{k_{el}}\right)\right]\left[1+\frac{k_{-dif}}{k_{el}}\left(1+\frac{k_{-el}}{k_{isc}^{51}}\right)\right]} \quad (23)$$

$$\alpha = 1 + k_{-el}/k_{en} \quad (24)$$

In order to estimate k_{isc}^{51}, one must look at the part of the data where it is most significant, i.e., at the lowest values of ΔG_{et}. If A is taken to be 10^{12} s^{-1} and the assumption is made that $k_{en} \approx k_\Delta \geq 2 \times 10^9$ s^{-1}, then $k_{el} = 10^{12}$ s^{-1} and $k_{-el} = 2 \times 10^9$ s^{-1} when ΔG_{et} is near −2 V. We can use $\langle k_q^{en}\rangle = 6.3 \times 10^9$ M^{-1}s^{-1} from Figure 4, and eq 23 reduces to eq 25.

$$k_q^{en} = \frac{1}{9}k_{dif} + \frac{5}{9}k_{dif}\frac{1}{1+\frac{k_{-dif}}{k_{el}}\left(1+\frac{k_{-el}}{k_{isc}^{51}}\right)} \quad (25)$$

Using the above values, one obtains $k_{isc}^{51} = 3.0 \times 10^7$ s^{-1}. This value is also not sensitive to the choice of A.

In the region of $\Delta G_{et} > -0.5$ eV, k_{isc}^{51} will be much smaller than k_{-el}, and the value of k_{en} can be estimated. Using $A = 10^{12}$ s^{-1}, $k_{el} = k_{-el} = 2.3 \times 10^{11}$ s^{-1} when $\Delta G_{et} = 0$. Using the above value of k_{isc}^{51} and $\langle k_q^{en}\rangle = 1 \times 10^9$ s^{-1} from Figure 4, simplified eq 26 is obtained. From this is obtained a reasonable value of $k_{en} = 1.8 \times 10^{10}$ s^{-1}. Again, this value is insensitive to variation in assumptions of A, and the value obtained is completely consistent with the assumption made above.

$$k_q^{en} = \frac{1}{9}k_{dif}\frac{1+\alpha\frac{k_\Delta}{k_{el}}}{1+\alpha\left(\frac{k_\Delta + k_{-dif}}{k_{el}}\right)} \quad (26)$$

The values one obtains for these physical parameters are obviously dependent on the kinetic model one chooses, and it is more than reasonable to argue that Scheme 2b is fundamentally flawed in not including other intersystem crossing paths, each with its own rate constant. However, the current and literature data justifies the assumption that the intersystem crossing rate constants are not, in general, large. We cannot comment specifically on the rates of singlet−triplet or triplet−quintet intersystem crossing; it is our intention that what we call k_{isc}^{51} represents a net flow from the quintet to the singlet manifold. The experimental results show that there is a net flow out of the quintet manifold for this series of compounds, but it is also clear that intersystem crossing is not exceedingly fast; otherwise values of ^3k_q would be much closer to k_{dif}. The question about the value of intersystem rate constant between quintet and triplet states of exciplex must remain open for discussion. For the best electron donors in our set with $\Delta G_{et} < -1.2$ eV (i.e., the plateau in Figure 2) the averaged value of the charge transfer quenching rate constant $\langle k_q^{CT}\rangle = 1.2 \times 10^{10}$ M^{-1} s^{-1}, while the expected limiting value of the quenching rate constant through process 13b is $k_{q,max}^{CT} = (1/3)k_{dif} = 1.1 \times 10^{10}$ M^{-1} s^{-1}, obviously identical within experimental error. Even then, the best fit for Figure 2 with eq 15 was obtained with a maximum plateau of 1.4×10^{10} M^{-1} s^{-1}. Thus, the experimental data point out that quintet−triplet interconversion probably takes place with some efficiency, but a quantitative estimate cannot be obtained.

Conclusion

An exciplex with partial charge transfer character is formed in the quenching of triplet states or amines and other aromatic hydrocarbons by molecular oxygen in nonpolar solvents. By measuring the total quenching rate constants and separating it into singlet and triplet channel components, it is shown that intersystem crossing must occur among the charge transfer complexes. Using a simplified kinetic model, a rate constant of 3×10^7 s^{-1} for the net intersystem crossing from the quintet exciplex to the singlet has been found. While intersystem crossing in the exciplex has been proposed previously, the current data are, to the best of our knowledge, the first that imply involvement of quintet complexes in quenching events.

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