Charge-Transfer Quenching of Singlet Oxygen $O_2(^1\Delta_g)$ by Amines and Aromatic Hydrocarbons

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The quenching rate constants of singlet oxygen $O_2(^1\Delta_g)$ luminescence at 1.27 μm by 29 amines and aromatic hydrocarbons were measured in acetonitrile and benzene. Quenching occurs via reversible charge transfer with the formation of an exciplex with a partial ($\delta \approx 0.2$ esu) electron transfer. An estimate of the intersystem-crossing rate constant for the exciplex of ca. 10^{10} s^{-1} is obtained, and a modest decrease with increasing exciplex energy is noted. The data predict and it is confirmed that charge transfer plays a significant role in the nonradiative decay of singlet oxygen in solvents as difficult to oxidize as toluene-d_8 and mesitylene. It is also confirmed that *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylene diamine quenches $O_2(^1\Delta_g)$ nearly exclusively by full electron transfer in D_2O, but electron transfer is not observed in other solvents.

Introduction

Interactions between molecular oxygen in its metastable $^1\Delta_g$ state and various organic molecules follow several different courses that result in either chemical transformations or physical quenching of $O_2(^1\Delta_g)$.[1−4] Literally thousands of solution-phase singlet-oxygen quenching rate constants have been compiled by now,[5] and one of the well-recognized mechanisms for physical quenching by certain electron-rich systems is known as charge transfer. In this pathway, there is formation of a $^1(\text{Quencher}^{\delta+}\cdots O_2^{\delta-})$ exciplex that decays to ground-state compounds.[1−3,5−9] As early as 1968, it was proposed that quenching of singlet oxygen by 1,4-diazabicyclo[2,2,2]octane (DABCO) in solution was through this mechanism,[10] and amines of various structural types have been studied since then.

Though steric factors can come into play in determining relative rates, a logarithmic dependence of $O_2(^1\Delta_g)$ quenching rate constants (k_q) on the ionization potential of aliphatic amines is known both in the gas phase[11,12] and in solution.[13−16] Quenching rate constants have been shown to correlate with Hammett σ values for a series of dimethylanilines, also consistent with a charge-transfer interaction.[17] Related nitrogen-containing functional groups also quench $O_2(^1\Delta_g)$. Hydrazines are known as excellent physical charge-transfer quenchers,[9] but sulfenamides (R−S−NR$_2$) quench singlet oxygen through reactive pathways.[18,19] In addition to nitrogen-based functionalities, various hydroquinones, phenols, and methoxybenzenes also physically quench $O_2(^1\Delta_g)$ with rate constants that depend on ease of oxidation.[16,20,21]

The key intermediates in the quenching pathways, exciplexes of singlet oxygen, are not very well characterized. Some years ago, Foote estimated that the $^1(O_2^{\delta-}\cdots\text{phenol}^{\delta+})$ exciplex in methanol involves 44% of the charge transfer expected for full electron transfer.[16] Recently, semiempirical molecular orbital calculations were performed for the $^1(O_2^{\delta-}\cdots\text{amine}^{\delta+})$ exciplex with aliphatic amines, and it was estimated that $\delta \approx 0.3$ esu.[22] We report an estimate of the degree of charge transfer in the $^1(O_2^{\delta-}\cdots\text{aniline}^{\delta+})$ exciplex based on the quenching of $O_2(^1\Delta_g)$ luminescence by aromatic amines in acetonitrile. These compounds were chosen in part because the oxidation potentials of such quenchers are generally reversible and, therefore, thermodynamically significant. We also derive an estimate of the rate of intersystem crossing back to the ground-state compounds for these complexes. Hydrocarbon quenchers also follow a similar pattern of k_q vs $\Delta G_{\text{e.t.}}$, and this is shown to be useful in predicting charge-transfer quenching by certain hydrocarbon solvents.

The process of exciplex formation[23−36] and its relationship to Marcus electron-transfer theory[37−39] is established.[26,40−42] For example, in their landmark paper,[24] Rehm and Weller explained that the quenching of aromatic hydrocarbon fluorescence by amines proceeded through the formation of exciplexes and presented their famous relationship between the quenching rate constant and the energy of full electron transfer. Our analysis of the quenching of $O_2(^1\Delta_g)$ by aromatic amines and hydrocarbons will also begin with this approach.

Experimental Section

Measurements were carried out in air-saturated solutions at ambient temperature, 23 °C. Absorption spectra were recorded on a UV-2101 PC Shimadzu spectrophotometer. Solvents were the purest grade commercially available and used as received, as were the perdeuterated compounds. All other materials were available commercially and purified as necessary by recrystallization and sublimation.

The $O_2(^1\Delta_g)$ luminescence at 1.27 μm was recorded with a high-sensitivity Ge detector with a response time <1 μs described elsewhere.[43] The second harmonic of a Nd:YAG laser Surelite I (532 nm, 5 ns, 2−7 mJ) was used for the excitation of sensitizers to produce $O_2(^1\Delta_g)$. The optical densities of solutions in a quartz cell (1 × 1 cm) were 0.1−0.2 at 532 nm.

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TABLE 1: Rate Constants of Singlet Oxygen Quenching

	acetonitrile			benzene	
quencher	$E_{1/2}^{\mathrm{ox}}$ (V, SCE)[a]	ΔG_{et} (eV)	k_q ($M^{-1}\,s^{-1}$)	k_q ($M^{-1}\,s^{-1}$)	k_r ($M^{-1}\,s^{-1}$)
TMPD	0.16[b]	−0.06	5.2×10^9	2.6×10^9	
p-phenylenediamine	0.18	−0.04	2.8×10^{10}	2.9×10^9	
p-aminodiphenylamine	0.27	0.05	1.1×10^9	1.2×10^8	
N,N-diphenyl-*p*-phenylenediamine	0.335	0.115	4.5×10^8	6.4×10^7	
N,N,N′,N′-tetramethylbenzidine	0.43	0.21	1.8×10^9	2.7×10^8	
o-phenylenediamine	0.40[b]	0.18	8.0×10^8	1.0×10^7	
2-aminoanthracene	0.44	0.22	2.3×10^8	3.1×10^7	
1-naphthylamine	0.54	0.30	2.7×10^8	7.3×10^6	
N,N-dimethyl-*p*-toluidine	0.65	0.43	1.0×10^9	1.5×10^8	
N,N-dimethylaniline	0.71	0.49	2.85×10^8	5.5×10^7	
diphenylamine	0.83	0.61	1.8×10^7	2.5×10^5	
N-methyl-*N,N*-diphenylamine	0.84	0.62	4.1×10^6	6.0×10^5	
aniline	0.87[c]	0.65	1.06×10^7	2.9×10^5	
p-iodoaniline	0.88[c]	0.66	5.1×10^6	6.0×10^6	
p-bromoaniline	0.89[c]	0.67	7.1×10^6	1.25×10^6	
p-chloroaniline	0.90[c]	0.68	7.6×10^6	1.5×10^5	
triphenylamine	0.92	0.70	4.1×10^7	1.9×10^5	
N,N-dimethyl-*p*-nitroaniline	1.19	0.97	1.1×10^6	2.5×10^5	
1,2,4-trimethoxybenzene	1.12[d]	0.90	4.4×10^7	1.1×10^7	$<5 \times 10^4$
1,4-dimethoxybenzene	1.34[d]	1.12	6.4×10^6	1.6×10^6	$<5 \times 10^4$
1,2,3-trimethoxybenzene	1.42[d]	1.20	1.7×10^5	4.4×10^4 [e]	
1,2-dimethoxybenzene	1.45[d]	1.23	7.4×10^5	2.1×10^5	$<1 \times 10^4$
hexamethylbenzene	1.46[g]	1.24	6.4×10^6	2.0×10^6	$<5 \times 10^4$
1,3-dimethoxybenzene	1.49[d,f]	1.27	2.2×10^5	6.2×10^4	$<1 \times 10^4$
1,3,5-trimethoxybenzene	1.49[d]	1.27	2.6×10^5	4.6×10^4	
pentamethylbenzene	1.58[g]	1.36	1.2×10^6	3.5×10^5	
1,2,4,5-tetramethylbenzene	1.59[g]	1.37	3.2×10^5	1.1×10^5	
1,2,4-trimethylbenzene	1.71[g]	1.49	4.1×10^4	1.6×10^4	
anisole	1.76[d]	1.54	1.5×10^4	5.4×10^3	$<5 \times 10^3$

[a] Reference 53. [b] Reference 67. Obtained from the oxidation potential vs AgCl by subtracting 0.04. [c] Reference 68. [d] Reference 69. [e] Reference 50. [f] Reference 70. [g] Obtained from the oxidation potential vs Ag/Ag^+ 0.01 M $AgNO_3$ in ref 53 by adding 0.30 V as recommended in ref 71.

The sensitizers were tetraphenylphorphine (TPP) in benzene and methylene blue (MB) in acetonitrile. Spectra and decay kinetics of transients were recorded by nanosecond laser photolysis as previously described.[44] Error limits for each rate constant are estimated to be ±15%. Thermodynamic parameters were determined over the range 10−70 °C.

The rate constants for the chemical reaction (k_r) of $O_2(^1\Delta_g)$ with aromatic hydrocarbons were estimated in benzene,[45] using anthracene in benzene, with $k_r = 1.5 \times 10^5\ M^{-1}s^{-1}$ as a standard.[46] The steady-state photolyses of air-saturated solutions of the sensitizer (TPP) and anthracene or aromatic hydrocarbon were carried out with $\lambda > 500$ nm using a 75 W xenon lamp and an appropriate cutoff filter. The TPP concentration was equal in all experiments. The consumption rates of anthracene and test compounds were estimated by UV analysis at appropriate long-wavelength absorption maxima.

Results

With the goal in mind of examining singlet-oxygen quenching by a series of compounds with a wide range of oxidation potentials, series of amines, alkylbenzenes, and alkoxybenzenes were chosen. Alkoxy compounds were chosen over phenols to reduce chemical reactivity.[2,3]

The decay kinetics of $O_2(^1\Delta_g)$ luminescence in pure solvents were first order, and the lifetimes agreed well with literature data.[5] The addition of amines or aromatic hydrocarbons as quenchers (Q) led to a decrease of the singlet-oxygen lifetime, with decay kinetics described by the usual first-order eq 1.

$$\tau_{\mathrm{obs}}^{-1} = \tau_{\mathrm{o}}^{-1} + k_q[\mathrm{Q}] \qquad (1)$$

The series of k_q values were obtained in CH_3CN and benzene and are listed in Table 1. As defined here, k_q included both physical and chemical quenching, though it is assumed that the physical quenching strongly predominates in nearly all cases. The few rate constants in Table 1 which have appeared in the literature agree well with the present determinations.[5,47−50]

Efforts were made to verify that the major term in k_q was physical quenching. When $O_2(^1\Delta_g)$ was quenched by amines in benzene or by aromatic hydrocarbons in either solvent, the formation of radical cations of the quencher was not observed. However, in air-saturated acetonitrile, the formation of amine radical cations was observed within the lifetime of the sensitizer triplet. The saturation of these solutions with O_2 led to a sharp decrease of the yield of radical cations. It was, thus, concluded that the radical cation formation was due to a direct quenching interaction between the sensitizer and the amines, though it is not possible to rule out a small contribution from electron transfer between from the amine to $O_2(^1\Delta_g)$.

The rate constants for chemical reaction of $O_2(^1\Delta_g)$ with selected aromatic hydrocarbons and alkoxyaromatics in benzene were measured by observing the permanent change in the UV spectrum as a function of time in steady-state irradiations. They were sufficiently low and difficult to measure, and only upper limits are given in Table 1. With the possible exception of anisole, the k_r values are much smaller than the k_q values and quenching of $O_2(^1\Delta_g)$ is almost entirely physical under these conditions. This is in agreement with previous observations using various methoxybenzenes as quenchers.[20,51,52] These authors did not find any traces of the oxidation products for

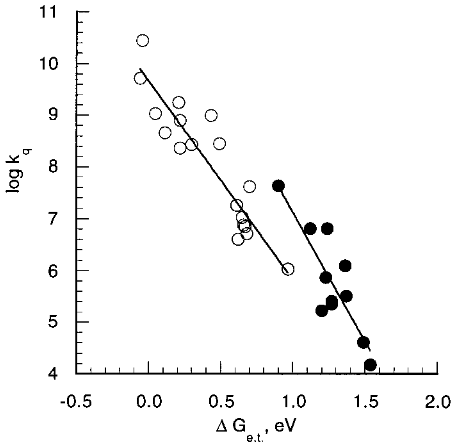


Figure 1. Dependence of $O_2(^1\Delta_g)$ quenching rate constant on free energy of complete charge transfer in acetonitrile: (○) amines; (●) CHO compounds.

compounds with oxidation potentials greater than 1.24 V vs SCE and found only a low rate of oxygenation of 1,2,4-trimethoxybenzene.

In acetonitrile, the free energy of electron transfer can be estimated according to the Rehm−Weller equation

$$\Delta G_{e.t.} = E_{1/2}^{ox}(A/A^{\bullet+}) - E_{1/2}^{red}(O_2/O_2^{\bullet-}) - E_o(^1\Delta_g) - \frac{e^2}{a\epsilon} \qquad (2)$$

where $E_{1/2}^{ox}(A/A^+)$ is the half-wave oxidation potential of the quencher, $E_{1/2}^{red}(O_2/O_2^-) = -0.82$ V,[53] and $E_o(^1\Delta_g) = 0.98$ eV,[54] the excitation energy of $O_2(^1\Delta_g)$. Redox potentials throughout this paper are taken from the literature and are relative to SCE in CH_3CN. The final term in eq 2 is the energy of the Coulombic interaction between the two ions formed after the electron transfer with internuclear distance a in the encounter complex. In acetonitrile, with a dielectric constant $\epsilon = 37.5$ and assuming the separation $a = 7$ Å,[24] this term is 0.06 eV. Rate constants for quenching versus $\Delta G_{e.t.}$ calculated this way are shown in Figure 1.

Thermodynamically meaningful oxidation potentials are not available for these quenchers in benzene. Though various attempts have been made in the literature to approximate oxidation potentials in various solvents based on the value from a single solvent, we did not believe any of them to be sufficiently reliable to give useful $\Delta G_{e.t.}$ values (see below). Therefore, in Figure 2, the quenching rate constants in benzene are simply plotted against the oxidation potentials obtained in acetonitrile.

The activation enthalpies for quenching of $O_2(^1\Delta_g)$ by aniline and triphenylamine in acetonitrile and benzene were measured. All of the apparent activation enthalpies were −0.5 ± 0.1 kcal/mol. These results are consistent with quenching by formation of exciplexes in a rapid preequilibrium regime.[1−3,41,55]

In analogy to the previous work of Foote,[56] the interaction of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) with $O_2(^1\Delta_g)$ was studied in D_2O. This is an exceptional case, in which full electron transfer (i.e., formation of superoxide and $TMPD^{\bullet+}$, Würster's Blue) is observed. Würster's blue was identified by its characteristic absorption spectrum.[57] In the determination of a rate constant for this reaction, the points due to observation of the growth of Würster's blue fell on a common line with those due to observation of $O_2(^1\Delta_g)$ phosphorescence, as shown in Figure 3. This coincidence demonstrates that the predominant process is chemical quenching by full electron transfer, shown in eq 3. A rate constant of 2.9 × 10^8 M^{-1} s^{-1} was obtained.

$$O_2(^1\Delta_g) + TMPD \rightarrow O_2^{\bullet-} + TMPD^{\bullet+} \qquad (3)$$

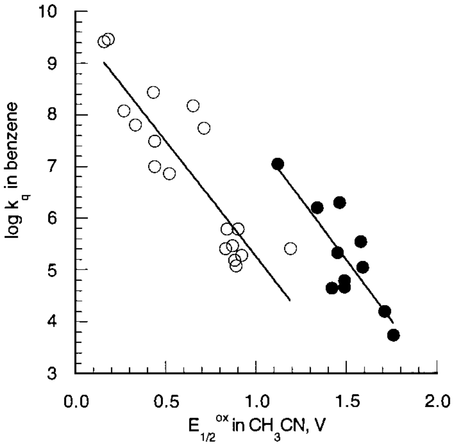


Figure 2. Rate constants of singlet-oxygen quenching in benzene plotted against oxidation potentials measured in acetonitrile: (○) amines; (●) CHO compounds.

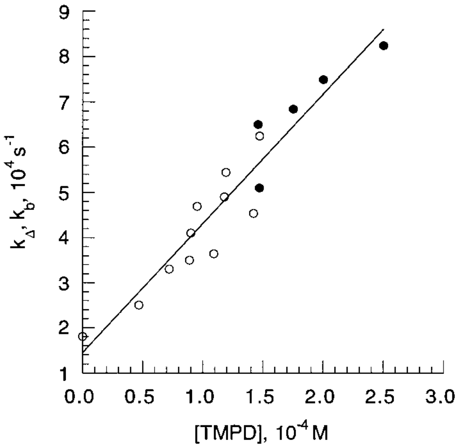


Figure 3. Dependence of $O_2(^1\Delta_g)$ decay rate constant (○) and rate constant of build-up of Wurster's blue absorption at 550 nm (●) on concentration of TMPD in D_2O.

TABLE 2: Quenching Rate Constants of Singlet Oxygen by TMPD in Different Solvents

solvent	ϵ	k_q (10^9 M^{-1} s^{-1})
hexane	1.89	0.49
CCl_4	2.24	0.74
benzene	2.28	2.6
toluene	2.38	2.0
diethyl ether	4.34	1.1
chloroform	4.81	0.67
tetrahydrofuran	7.58	2.9
CH_2Cl_2	8.93	2.1
acetone	20.7	3.2
acetonitrile	37.5	5.2

Perhaps surprisingly, similar radical cations were not observed for other related amines, even *p*-phenylenediamine. The quenching of $O_2(^1\Delta_g)$ by TMPD was also examined in a series of non-hydroxylic solvents; in no other case was Würster's blue observed. The data are given in Table 2.

To probe for possible heavy-atom effects in some of the data, several halogenated anilines with similar oxidation potentials were used as quenchers. As can be seen in Table 3, any heavy-atom contribution to the observed rate constant k_q is kinetically irrelevant, at least in acetonitrile.

TABLE 3: Singlet-Oxygen Quenching Rate Constants for Halogenated Anilines

	acetonitrile		benzene
solvent	$E_{1/2}^{ox}$ (vs SCE)[75]	k_q (10^6 M^{-1} s^{-1})	k_q (10^6 M^{-1} s^{-1})
aniline	0.87	10.6	0.29
4-chloroaniline	0.90	7.6	0.15
4-bromoaniline	0.89	7.1	1.25
4-iodoaniline	0.88	5.1	6.0

Finally, $O_2(^1\Delta_g)$ lifetimes were measured in several additional pure solvents, including perdeuterated solvents (Table 4). To ensure that impurities in the deuterated solvents did not interfere with the singlet-oxygen lifetime measurements, the lifetimes of the TPP and C_{60} triplets were measured in the absence of oxygen. They were quite similar to values obtained from highly purified nondeuterated solvents. Additionally, NMR analysis showed that there was not significant contamination from H_2O or the protonated solvents themselves. The values for perdeuterated benzene and toluene were in good agreement with previous reports.[5]

Discussion

Rate Constants and Charge Transfer. Though there is scatter in the data, the plots of log k_q in Figures 1 and 2 can be fit to linear equations. Slopes, intercepts, and standard errors were determined. Separate fits were done for the amines and hydrocarbons in CH_3CN and benzene solvents, though at least in acetonitrile a single fit also appeared satisfactory. We based this decision on the idea that it is likely that there is a specific N···O_2 interaction in the amines which does not exist for the other compounds. Also, it is apparent in benzene solvent that a separate fit is necessary. Finally, previous work using indirect methods suggested that separate lines were justified for amines, methoxybenzenes, and phenols.[16]

$$\log k_q = 9.7\ (\pm 0.2) - 3.8\ (\pm 0.4)\Delta G_{e.t.} \qquad \text{(amines, acetonitrile, } R = 0.92) \quad (4a)$$

$$\log k_q = 9.7\ (\pm 0.4) - 4.5\ (\pm 0.6)E_{1/2}^{ox} \qquad \text{(amines, benzene, } R = 0.89) \quad (4b)$$

$$\log k_q = 12.1\ (\pm 1.3) - 5.0\ (\pm 1.0)\ \Delta G_{e.t.} \qquad \text{(hydrocarbons, acetonitrile, } R = 0.86) \quad (5a)$$

$$\log k_q = 12.2\ (\pm 1.6) - 4.7\ (\pm 1.0)E_{1/2}^{ox} \qquad \text{(hydrocarbons, benzene, } R = 0.83) \quad (5b)$$

It is reasonable to ascribe some of the greater deviation in fit for Figure 2 to the arbitrary use of the acetonitrile-based oxidation potentials. Furthermore, because of the smaller range of data and large standard errors for the aromatic hydrocarbons, the quantitative analysis below will be restricted to the case of the amines in acetonitrile. However, the qualitative predictive usefulness of the present hydrocarbon data will also be demonstrated.

Steric factors do not play a large role in determining rate constants for these compounds. An examination point by point from Table 1 does not show a pattern of rate constants for bulky quenchers (e.g., triphenylamine) being consistently below the fitted line.

Using any version of the Marcus or Rehm–Weller theories, a plot of log k_q against ΔG should curve as the reaction becomes exothermic and/or as the rate constants approach the diffusion-controlled limit. However, the current data are modeled by endergonic electron transfer, are below diffusion control, and do not warrant fitting to any nonlinear function. The limiting slope for full electron transfer in the absence of steric effects should approach $-(2.3RT)^{-1}$, or -17.0 eV^{-1}.[24] The obtained slopes are considerably below this limit.

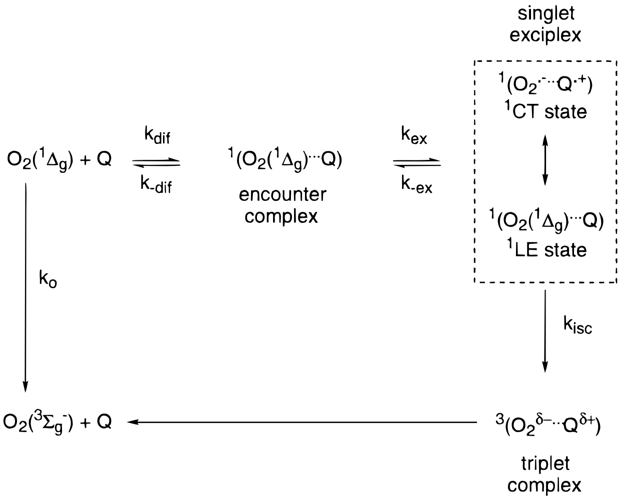
Following the treatment used previously by several authors,[58−61] the degree of charge transfer in the $^1(O_2^{\delta-}\cdots Q^{\delta+})$ exciplex (i.e., the value of δ) can be estimated by dividing the observed slope

TABLE 4: $O_2(^1\Delta_g)$ Lifetimes with E→V and Charge-Transfer Contributions

solvent	IP (eV)[a]	$E_{1/2}^{ox}$ (V)[a]	τ_Δ^{obs} (μs)	$\tau_\Delta^{e\to v}$ (μs)[b]	k_Δ^{obs} (10^3 M^{-1} s^{-1})[c]	$k^{e\to v}$ (10^3 M^{-1} s^{-1})[b]	$k_{q,ct}^{obs}$ (10^3 M^{-1} s^{-1})[d]	$k_{q,ct}^{fit}$ (10^3 M^{-1} s^{-1})[e]
1,2,4-trimethoxybenzene	7.5[f]	1.12	<1	35	>150	4.3	>150	10 000
1,2-dimethoxybenzene	7.9[f]	1.45	<1	34	>130	3.8	>130	270
1,3-dimethoxybenzene	8.0[f]	1.49	1.9	34	69	3.8	65	170
phenyl ether	8.09		17	32	9.3	4.9	4.4	
1,2,4-trimethylbenzene	8.27	1.71	9.5	35	14.2	4.3	9.9	16
anisole	8.21	1.76	9.8	32	11	3.4	7.6	9.4
anisole-*d*8			12.5	775	8.7	0.14	8.6	9.4[g]
mesitylene	8.41	1.80	15	33	9.3	4.3	5.0	6.1
mesitylene-*d*12			28	880	5.0	0.16	4.8	6.1[g]
p-xylene	8.44	1.77	19	32	6.4	3.8	2.6	8.5
p-bromoanisole	8.49	1.70	16	43	7.8	2.9	4.9	18
p-chloroanisole	8.5[f]	1.72	15	42	8.2	2.9	5.3	15
toluene	8.82	1.98	30	31	3.5	3.4		0.9
toluene-*d*8			290	761	0.36	0.14	0.2	0.9[g]
benzene	9.25	2.3	30	30	3.0	3.0		0.03
benzene-*d*6	9.25[h]		650	680	0.14	0.13		0.03[g]
acetone[a]	9.71		51[i]	40	1.4	1.9		
cyclohexane[a]	9.86		23[i]	29	4.7	3.7		
pentane[a]	10.35		34[i]	31	3.4	3.7		
methanol[a]	10.85		9.4[i]	13	4.3	3.1		

[a] All lifetimes measured in this work unless noted otherwise. All values are in good agreement with previous reports where available.[5] IPs from ref 72. Oxidation potentials vs SCE in acetonitrile from refs 53, 68, and 69. [b] Calculated according to the equations of Schmidt and Afshari taking into account only E−V energy transfer.[66] [c] Molar quenching rate constant derived from τ_Δ and solvent molarity. [d] $k_{q,ct}^{obs} = k_\Delta^{obs} - k^{e\to v}$. [e] e $k_{q,ct}^{fit}$ is derived from the hydrocarbon data in Figure 2 (i.e., eq 5b) and oxidation potentials. [f] Ionization potential estimated by comparison to the oxidation potentials of related compounds with known ionization potentials. [g] Assumes oxidation potential of perdeuterated solvent is the same as protonated material. [h] Reference 73. [i] Reference 66.

SCHEME 1



by 17.0 eV. This yields a value of 0.22 for δ for the amines in acetonitrile. This method assumes a constant charge transfer over the whole series, which is undoubtedly a simplification, but it provides a reasonable qualitative experimental estimate. The wave function of the exciplex can be represented as the mixture of wave functions of a locally excited state (^{1}LE) and singlet ion−radical pair (^{1}CT), as in eq 6, with $\alpha^2 \approx 0.8$ and $\beta^2 \approx 0.2$. Using a similar method, Foote estimated a charge

$$\Psi(^1\text{Ex}) = \alpha\Psi(^1\text{LE}) + \beta\Psi(^1\text{CT}) \qquad (6)$$

transfer of 0.44 esu for a series of phenols in methanol;[16] our data yield $\delta = 0.29$ for the hydrocarbons and methoxybenzenes in acetonitrile.

Estimate of k_{isc} for the Exciplexes. A kinetic scheme based on Rehm and Weller's original two-stage steady-state approach for the quenching process is shown in Scheme 1.[24] A rate constant is not assigned to the dissociation of the triplet complex, as this is expected to be fast and the previous step is irreversible. Given this scheme and the observed kinetic data, an estimate of the intersystem-crossing rate of the exciplex, k_{isc}, can be made.

Applying the steady-state approximation to both the singlet encounter complex and the singlet exciplex and rearranging appropriately, one arrives at eq 7, where ΔG_{ex} is the free-energy difference between the encounter complex and the singlet exciplex (taken to be $0.22\Delta G_{e.t.}$), k_q is the observed quenching rate constant, and k_{dif} for molecular oxygen is 3.7×10^{10} M^{-1} s^{-1}.[62] A is the preexponential factor for k_{ex}, and $\Delta G_{ex}^{\ddagger}$ is the

$$k_{isc} = \frac{\exp(\Delta G_{ex}/RT)}{0.86(k_q^{-1} - k_{dif}^{-1})M^{-1} - A^{-1}\exp(\Delta G_{ex}^{\ddagger}/RT)} \qquad (7)$$

activation energy for the same reaction. A more complete derivation is given in the Appendix.

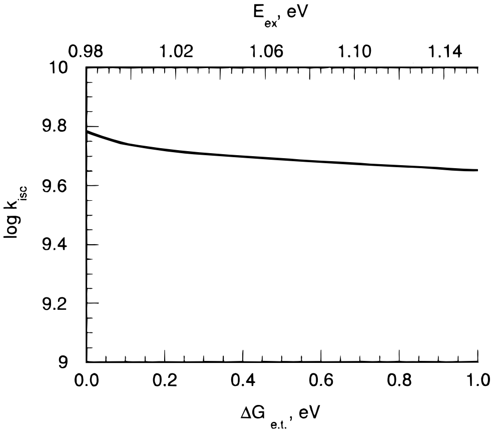


Figure 4. Estimated rate of intersystem crossing in acetonitrile from the singlet exciplex plotted against exciplex energy (E_{ex}) and energy of full electron transfer ($\Delta G_{e.t.}$).

Using eq 4a to relate k_q to ΔG_{ex}, a qualitative estimate of k_{isc} can be made, as shown in Figure 4. To achieve this, a value for the preexponential factor A must be selected. Intuitively, one expects the activation entropy to be negative because the exciplex should be more "organized" than the simple encounter complex. However, k_{isc} from eq 7 is actually quite insensitive to A for any value from 10^{11} to 10^{15}; a value of 10^{13} was used to generate Figure 4. The salient conclusion from Figure 4 is that k_{isc} is not a sharp function of the energy of the exciplex ($E_{ex} = 0.98$ eV $+ \delta\Delta G_{e.t.}$) in the range of the current data and is about 5×10^9 s^{-1}.[63] Minaev's analysis suggests that k_{isc} should increase as the charge-transfer character of the exciplex increases as a result of increased spin−orbit coupling.[64] These results are in qualitative agreement with that conclusion. The already fast k_{isc} values due to the inherently strong spin−orbit coupling of the system are a reasonable explanation for why a relatively small perturbation from a heavy-atom effect in the haloanilines is not observed.

The observed rate constants k_q vary over a much wider range than k_{isc} in a given series. The greater portion of this derives from the energy of the exciplex, i.e., quenching is slower when exciplex formation is slightly endothermic.

One can use the present data to provide an order-of-magnitude estimate of the lifetime of the singlet exciplex using eq 8. From

$$\tau_{ex} = (k_{isc} + k_{-ex})^{-1} \qquad (8)$$

the value of ΔG_{ex} and k_{ex} (see Appendix), k_{-ex} may be obtained. Its analytical form is $A\exp[(\delta\Delta G_{e.t.} - \Delta G_{ex}^{\ddagger})/RT]$. Over the range of $\Delta G_{e.t.} = 0-1$ eV, the exponential term varies from about 0.017 to 0.14. Thus, if A is taken as 10^{13} s^{-1}, k_{-ex} ranges from 1.7×10^{11} to 1.4×10^{12} s^{-1}. Different assumptions about A will lead to correspondingly different values of k_{-ex}. Regardless, for reasonable values of A, $k_{-ex} \geq k_{isc}$ and τ_{ex} is expected to in the picosecond regime.

Charge-Transfer Quenching by Solvents. One of the consequences of the data in Figures 1 and 2 is that charge-transfer quenching may be an important contributor to the nonradiative decay of $O_2(^1\Delta_g)$ in certain solvents that are chemically unreactive. This is in addition to the usual electronic to vibrational (E−V) energy transfer.[65]

Schmidt and Afshari proposed a very successful semiempirical equation to estimate the $O_2(^1\Delta_g)$ rate constant for E−V quenching ($k^{e\rightarrow v}$) and thus the singlet-oxygen lifetime ($\tau_\Delta^{e\rightarrow v}$) when only energy transfer from singlet oxygen to the vibrational levels of solvent molecules occurs.[66] Such rate constants are tabulated in Table 4, along with experimental values of total singlet-oxygen quenching.

The E−V expression works very well for solvents that are poor electron donors, i.e., those with ionization potentials larger than about 8.5 eV. Obviously, methoxybenzenes have a significant charge-transfer quenching component. However, the data in Table 4 indicate that solvents such as mesitylene also quench largely by charge transfer. An estimate of the charge-transfer component of the quenching ($k_{q,ct}^{obs}$) is made by subtracting the calculated E−V component from the observed total quenching rate constant.

Lifetime data from deuterated solvents support this analysis. A critical result of the E−V mechanism is that C−D and O−D bonds are significantly poorer energy acceptors than C−H and O−H bonds. Thus, the comparison of singlet-oxygen lifetimes in solvents and their perdeuterated analogues is an excellent probe for quenching mechanisms beyond E−V energy transfer. The very similar singlet-oxygen lifetimes in mesitylene and mesitylene-d_{12}, for instance, prove that another mechanism is responsible for the lifetime limitation. We assert that this is charge-transfer quenching. Further, this explanation offers a reason for the poor prediction of τ_Δ in toluene-d_8 by the E−V mechanism. It serves as a critical case where a charge-transfer component to quenching is just competitive with $k^{e\rightarrow v}$. With more solvents that are more difficult to oxidize (e.g., benzene), the usual E−V mechanism is dominant and the lifetimes of $O_2(^1\Delta_g)$ are well predicted in the protonated and deuterated isotopomers.

An independent estimate of $k_{q,ct}$ can be made from extrapolation of the fit for the hydrocarbon data in benzene (i.e., eq 5b). This is given as $k_{q,ct}^{fit}$ in Table 4, and the agreement between the two estimates of $k_{q,ct}$ is quite good given the methods used.

Solvent Effects. It would be quite useful to be able to predict the rate constant for charge-transfer quenching in a given arbitrary solvent from the redox and kinetic data in acetonitrile. To do so, one would need to be able to predict the thermodynamically meaningful redox potentials and solvation energies (relative to acetonitrile) in the new solvent. Indeed, Weller developed an empirical correction for exciplex formation for comparing nonpolar solvents to acetonitrile, which replaced the Coulomb term in eq 2.[23] This results in the same shift in $\Delta G_{e.t.}$ for all quenchers and predicts, therefore, that the ratio of rate constants ($k_q^{CH_3CH}/k_q^{C_6H_6}$) should be quite similar in a related series. For the hydrocarbon quenchers, this is approximately the case, the ratios being between 2.6 and 4. However, for the amines, the ratio is much more variable, from just under 1 to over 200, with no obvious pattern. As a result, quantitative treatment of the benzene solvent case with eq 7 is not justified. Nonetheless, the utility of the fits in empirically predicting charge-transfer quenching by other solvents was demonstrated in the previous section.

Finally, we would like to comment on the quenching rate constant obtained for TMPD in several non-hydroxylic solvents (Table 2). These solvents were chosen to avoid strong specific interactions, hydrogen-bond donation in particular. It is clear that the rate constant increases with dielectric constant, but we thought it was desirable to model this behavior more quantitatively for a single compound over a series of solvents. Weller introduced another analysis, based on the Born equation, which takes into account the solvent dielectric constant, the exciplex dipole, and the Onsager radius of the exciplex.[30] Unfortunately, we were not able to apply this model successfully in any quantitative sense. With these data alone, it cannot be determined if that is due to an inherent shortcoming of the model or a more complex behavior of the system, such as dramatic changes in the degree of charge transfer (unlikely given the fairly similar slopes of eqs 4a and 5a) or exciplex geometry.

Summary

A steady-state analysis of a two-stage charge-transfer quenching mechanism of singlet oxygen is supported by slightly negative activation enthalpies. Use of an idealized linear relationship between log k_q and the oxidation potential of aromatic amines obtained allows an estimate of the intersystem-crossing rate constants (ca. 10^{10} s^{-1}) of the singlet exciplexes formed by aromatic amines and $O_2(^1\Delta_g)$ in acetonitrile. Similar data for aromatic hydrocarbons in benzene allow prediction and detection of charge-transfer quenching by solvents as difficult to oxidize as toluene-d_8. Charge-transfer quenching probably plays a part in limiting the singlet-oxygen lifetime in solvents with ionization potentials as high as approximately 8.8 eV.

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Appendix: Derivation of Eq 7

Equation 9 is obtained directly from Scheme 1 using successive steady-state approximations.[24] The equilibrium

$$k_q = k_{dif}\left(1 + \frac{k_{-dif}}{k_{ex}} + \frac{k_{-dif}}{k_{isc}K_{ex}}\right)^{-1} \tag{9}$$

constant $K_{ex} = k_{ex}/k_{-ex}$ and is for the formation of the singlet exciplex from the encounter complex. Rearrangement of eq 9 to solve for k_{isc} yields eq 10.

$$k_{isc} = K_{ex}^{-1}\left(\frac{k_{dif}}{k_{-dif}}(k_q^{-1} - k_{dif}^{-1}) - k_{ex}^{-1}\right)^{-1} \tag{10}$$

The equilibrium constant for exciplex formation K_{ex} is estimated with $\Delta G_{ex} = -\beta^2 (E_{LE} - E_{CT})$, with β^2 taken from the slope in eq 4a divided by 2.3RT.[59] This is used with the formulation of Rehm and Weller (eq 11) to obtain k_{ex} (eq 12).[24]

$$\Delta G_{ex}^{\ddagger} = \frac{\Delta G_{ex}}{2} + \left[\left(\frac{\Delta G_{ex}}{2}\right)^2 + \Delta G^{\ddagger}(0)^2\right]^{1/2} \tag{11}$$

In eq 11, $\Delta G^{\ddagger}(0)$ is taken to be 0.104 eV, as in the original work, but ΔG_{ex} is used in place of ΔG_{et}.

$$k_{ex} = A \exp(-\Delta G_{ex}^{\ddagger}/RT) \tag{12}$$

The values of k_{dif} for molecular oxygen are taken to be 3.7 × 10^{10} and 3.0 × 10^{10} M^{-1} s^{-1} in acetonitrile and benzene, respectively.[62] The value of $k_{dif/}k_{-dif}$ is taken to be 0.86 M^{-1}, given an assumption of an internuclear distance of 7 Å.[41] Finally, then, eq 7 is obtained for k_{isc}. Furthermore, it can be

$$k_{isc} = \frac{\exp(\Delta G_{ex}/RT)}{0.86(k_q^{-1} - k_{dif}^{-1})M^{-1} - A^{-1}\exp(\Delta G_{ex}^{\ddagger}/RT)} \tag{7}$$

shown that eq 7 reduces to the one steady-state limit of eq 13 if limiting assumptions are made about the magnitude of various terms in eq 7. Quite similar values of k_{isc} are thus obtained.

$$O_2(^1\Delta_g) + Q \underset{k_{-ex}}{\overset{k_{ex}}{\rightleftharpoons}} \underset{\text{exciplex}}{^1(O_2(^1\Delta g)\cdots Q)} \xrightarrow{k_{isc}} O_2(^3\Sigma_g^-) + Q$$

$$k_{isc} = k_q \exp(\Delta G_{ex}/RT) \tag{13}$$

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