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ARTICLES

Common Marcus Type Dependence of the Charge Transfer Induced Processes in the Sensitization and Quenching of Singlet Oxygen by Naphthalene Derivatives

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The charge-transfer induced quenching processes of the lowest excited triplet state (T_1) of naphthalene derivatives by ground-state oxygen and of singlet oxygen $O_2(^1\Delta_g)$ by ground state naphthalene derivatives have been investigated in three solvents of different polarity. Both deactivation processes are described by one common Marcus type plot. The analysis of the data strongly indicates that exciplexes with the same degree of average partial charge transfer (pCT) and the same reorganization energy are formed in the rate-determining step of both quenching processes. The free energies of pCT complex formation are related to the corresponding free energy of complete electron transfer by $\Delta G_{CT} = f\Delta G_{CET}$ with a common corrective factor f, for T_1 and $O_2(^1\Delta_g)$ deactivation. The reorganization energy increases from 34 kJ mol^{-1} in carbon tetrachloride to 92 kJ mol^{-1} in acetonitrile. The charge transfer character is shown to be significantly larger than 25% and to increase with increasing solvent polarity.

Introduction

Photosensitized processes involving molecular oxygen in its excited $^1\Delta_g$ state play a substantial role in numerous systems of chemical, biological, and medical interest, and have been thoroughly investigated since the early 1960s.[1−8] Charge transfer (CT) effects on the determining parameters of these processes have been considered as one major key to the understanding of the increasingly rich experimental data. Besides a few well-known reactive pathways, deactivation of $O_2(^1\Delta_g)$ most commonly proceeds via physical mechanisms. Both solution- and gas-phase studies left no doubt that for strongly electron-donating physical quenchers, the ubiquitous collisional electronic to vibrational (e−v) deactivation[9−14] is largely outweighed by a competing CT mechanism.[15−19] In these cases, the rate constant $k_\Delta{}^Q$ of singlet oxygen deactivation is mainly determined by the ability of the quencher to transfer electrical charge to the oxygen molecule in the deactivating collision, and correlates rather smoothly with its oxidation potential E_{ox} or its ionization energy. Competing processes have been observed to a very similar extent in the generation of singlet oxygen from excited triplet sensitizers. Very fast events, strongly deviating from the initially observed dependence of quenching rate constants $k_T{}^Q$ on the sensitizer triplet energy,[20] led Garner and Wilkinson to modify the classical scheme originally proposed by Gijzeman et al., envisaging the possibility of a significant contribution of CT pathways in the sensitization process.[21] Their assumption has been supported by several authors, and was quantitatively verified by numerous investigations including our own.[19,22−33] Thus, both quenching of excited triplet states by ground state

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oxygen and of excited singlet oxygen by singlet ground states are additionally composed of an energy transfer and a CT component. The latter has been correlated with the free energy change ΔG_{CET} for complete electron transfer to oxygen, which can be calculated by the Rehm−Weller equation:[34]

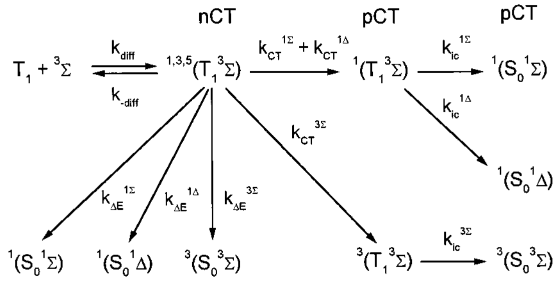
$$\Delta G_{\mathrm{CET}} = F(E_{\mathrm{ox}} - E_{\mathrm{red}}) - E_{\mathrm{exc}} + C \qquad (1)$$

F is the Faraday constant, E_{red} the reduction potential of molecular oxygen (−0.78 V vs SCE in acetonitrile),[35] E_{exc} is the excitation energy, i.e., the state energy E_{T} of the quenched sensitizer triplet, or the state energy $E_{\Delta} = 94$ kJ mol^{-1} of the quenched $O_2(^1\Delta_g)$. The electrostatic interaction energy C was often neglected when data from the same solvent were compared. Quantitatively significant studies were elegantly done on series of naphthalene and biphenyl derivatives, where the only property that varies noticeably with changing substituent is the oxidation potential.[23,27,29,30] Wilkinson and co-workers widely investigated singlet oxygen generation from those compounds, showing that a decrease in ΔG_{CET} makes this process considerably faster but significantly less efficient. Darmanyan et al. generalized these studies, demonstrating that even for hydrocarbons of very different structure, $k_{\mathrm{T}}^{\mathrm{Q}}$ depends in a surprisingly similar way on ΔG_{CET}.[31] However, this dependence was markedly weaker than expected for a complete electron transfer, and the authors largely agreed that only a partial CT is involved in these processes. Sensitizers of singlet oxygen are often electron-rich polyaromatic compounds and thus most likely to participate in a CT quenching of $O_2(^1\Delta_g)$ as well. Quantitative investigations of Darmanyan et al. showed that there is a very general dependence on ΔG_{CET} of the rate constant of $O_2(^1\Delta_g)$ deactivation by electron-donating quenchers.[18] They estimated that this pathway proceeds via exciplexes with a partial CT character of ca. 20%. On the basis of the striking similarity in the structures postulated for the CT exciplexes involved in both quenching of excited triplet states by ground-state oxygen and deactivation of excited singlet oxygen by singlet ground-state quenchers, we felt that common mechanisms may participate in these processes, and chose to investigate an extended series of naphthalene derivatives (NDs), as sensitizers and as quenchers of $O_2(^1\Delta_g)$ in three solvents of varying polarity, to clarify our minds on those parallelisms.

Experimental Section

Carbon tetrachloride (TET, Merck, p.a., Al_2O_3), phenalenone (PHE, Aldrich, 97%, silica gel/CH_2Cl_2), 1-methoxynaphthalene (1MEON, Fluka, 98+%, Al_2O_3), 1-bromonaphthalene (1BRN, Fluka, 97%, Al_2O_3), and *N*,*N*-dimethyl-1-naphthylamine (1DMAN, Aldrich, 99%, Al_2O_3) were purified by column chromatography. 1-Methylnaphthalene (1MEN, Aldrich, 95%) was distilled, benzophenone (BPH, Fluka, 98+%, ethanol), acenaphthene (ACEN, Aldrich, 97%, hexane), 2-methoxynaphthalene (2MEON, Aldrich, 99%, ethanol), naphthalene (NAPH, Fluka, 98+%, pentane), 1-cyanonaphthalene (1CNN, Aldrich, 98%, hexane), and 2-bromonaphthalene (2BRN, Aldrich, 97%, ethanol) were purified by crystallization. 2,6-Dimethylnaphthalene (26DMEN, Aldrich, 99%), 2-methylnaphthalene (2MEN, Aldrich, 98%), 2,3-dimethylnaphthalene (23DMEN, Aldrich, 98%), 2,6-dimethoxynaphthalene (26DMEON, Aldrich, 99%), 2,7-dimethoxynaphthalene (27DMEON, Aldrich, 98%), 1-fluoronaphthalene (1FN, Lancaster, 98%), dichloromethane (DCM, Merck, p.a.), acetonitrile (ACN, Fluka, >99.5%), and deuterated acetonitrile (Eurisotop, 99.8%) were used as received.

SCHEME 1

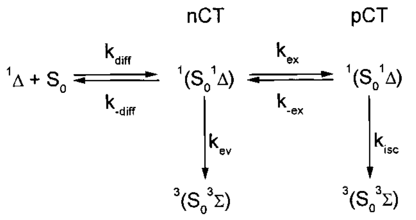


The setup used to monitor the rise and decay kinetics of $O_2(^1\Delta_g)$ has been described elsewhere.[36,37] Irradiation was provided by an excimer laser (Lambda Physik EMG 200) pumped dye laser (Lambda Physik FL 3002) at 409 nm, a Q-switched, frequency tripled Nd:YAG laser (Quantel Brilliant) at 355 nm or a XeCl-excimer laser (ATL Lasertechnik) at 308 nm. The $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ phosphorescence was recorded at 1275 nm using a cryogenic germanium diode (North Coast EO817P) and a transient digitizer (Tektronix TDS 3052). At least 20 shots were averaged for improved signal-to-noise ratios. In singlet oxygen quenching experiments, solutions of PHE were used as sensitizer. $O_2(^1\Delta_g)$ lifetimes were obtained from fits to the first-order decay profiles, and the rate constants for its quenching by the NDs from the slopes of the respective Stern−Volmer plots, whereby the data for ACN have been in part determined in the perdeuterated solvent. Rate constants for the oxygen quenching of excited triplet NDs were obtained from the rise of the $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ phosphorescence, as previously described.[38] Except for 26DMEON, which was directly excited at 308 nm, BPH was used as a primary sensitizer in solutions containing the respective ND at 0.05 M. The corresponding ACN data have been taken from Wilkinson et al.[29] All experiments were carried out in air-saturated solutions, at room temperature, which varied from 22 °C to 25 °C. Oxygen concentrations $[O_2]$ are directly proportional to the partial pressure p_{O_2} of O_2. We use for our data the following concentrations $[O_2]_1$ at $p_{O2} = 1$ bar: 10.7×10^{-3} M (DCM, 20 °C) and 12.4×10^{-3} M (TET, 20 °C)[39] and the temperature-dependent vapor pressure p_{v}, which amounts at 20 °C to 0.49 bar (DCM), and 0.12 bar (TET) and which has to be evaluated for the actual temperature from respective data collections.[40] Finally we calculate at atmosheric pressure p_{a} for air-saturated solutions $[O_2] = [O_2]_1 0.21(p_{\mathrm{a}} - p_{\mathrm{v}})$. Efficiencies S_{Δ} of $O_2(^1\Delta_g)$ generation refer to the well-established solvent independent value of 0.97 of the reference PHE.[41] They were obtained by comparison of excitation energy-normalized $O_2(^1\Delta_g)$ phosphorescence signals of sample and reference, which were both extrapolated to the time of laser pulse ignition. Triplet energies were determined by phosphorescence spectroscopy or photoacoustic calorimetry (PAC), using BPH as a primary sensitizer, as explained elsewhere.[41] Oxidation potentials were determined as previously described.[29]

Results

Scheme 1 is used to discuss the kinetics of the deactivation of triplet (T_1) states by $O_2(^3\Sigma_g^-)$ (= $^3\Sigma$). Encounter complexes with singlet, triplet and quintet multiplicity with no particular CT character (nCT) are formed. $^{1,3}(T_1{}^3\Sigma)$ nCT complexes decay by internal conversion (ic), with rate constants $k_{\Delta E}{}^{1\Sigma}$, $k_{\Delta E}{}^{1\Delta}$, and $k_{\Delta E}{}^{3\Sigma}$, to excited nCT complexes $^1(S_0{}^1\Sigma)$,$^1(S_0{}^1\Delta)$, and $^3(S_0{}^3\Sigma)$, which finally dissociate to yield ground-state sensitizer S_0 and $O_2(^1\Sigma_g^+)$ (=$^1\Sigma$), $O_2(^1\Delta_g)$ (=$^1\Delta$), and $O_2(^3\Sigma_g^-)$, respec-

SCHEME 2



tively.[33,42] The ic competes with the formation of exciplexes with partial CT character (pCT), i.e., $^1(T_1{}^3\Sigma)$ with rate constant ($k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta}$), or $^3(T_1{}^3\Sigma)$ with rate constant $k_{CT}{}^{3\Sigma}$. The ic of these exciplexes (with rate constants $k_{ic}{}^{1\Sigma}$, $k_{ic}{}^{1\Delta}$, and $k_{ic}{}^{3\Sigma}$) leads via pCT complexes $^1(S_0{}^1\Sigma)$,$^1(S_0{}^1\Delta)$, and $^3(S_0{}^3\Sigma)$ to the CT-induced formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g{}^-)$, respectively.[33] It has been shown that exciplex formation is the rate-determining step.[33]

No direct product channel exists for the quintet nCT complex, but $^5(T_1{}^3\Sigma)$ nCT could contribute to the singlet and triplet deactivation channels by isc to $^{1,3}(T_1{}^3\Sigma)$ nCT. If this isc process does not occur, the maximum rate constant of T_1 state quenching should be $^4/_9 k_{diff}$.[20,30] However, rate constants $k_T{}^Q \lesssim 0.64 k_{diff}$ exceeding the spin-statistical limit have already been determined.[26,31] Similarly, rate constants of overall singlet oxygen formation exceeding slightly but significantly the respective limit of $^1/_9 k_{diff}$ have been found by us with 4,4-dimethoxybiphenyl in TET at room temperature (+ 30%),[43] and by Grewer and Brauer with phenalenone and benzoylbiphenyl in low-temperature studies.[24] These findings indicate that at least in some cases the singlet and triplet channels may be additionally fed by the quintet complexes via intersystem crossing (isc). Therefore, we evaluate the overall rate constant $k_{D,T}$ of the deactivation of nCT complexes^{1,3,5} $(T_1{}^3\Sigma)$ by eq 2, assuming that these complexes are formed with rate constant k_{diff} and either dissociate back to T_1 and $O_2(^3\Sigma_g{}^-)$ with rate constant k_{-diff} or deactivate with rate constant $k_{D,T}$ to the products ground-state sensitizer S_0 and $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, or $O_2(^3\Sigma_g{}^-)$.

$$k_T{}^Q = k_{diff}\, k_{D,T}/(k_{-diff} + k_{D,T}) \qquad (2)$$

$k_{D,T} = k_{-diff}\, k_T{}^Q/(k_{diff} - k_T{}^Q)$ is obtained by rearranging eq 2. The overall rate constants of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ formation are given as $ak_{D,T}$, $bk_{D,T}$, and $(1 - a - b)k_{D,T}$, where a and b represent the efficiencies of direct formation of $O_2(^1\Sigma_g{}^+)$ and $O_2(^1\Delta_g)$, respectively. In the present investigation, we will focus on the triplet pCT deactivation channel, whose rate constant $k_{CT}{}^{3\Sigma}$ is obtained by subtracting the contribution of the nCT deactivation pathway from the overall rate constant of formation of $O_2(^3\Sigma_g{}^-)$, eq 3.

$$k_{CT}{}^{3\Sigma} = k_{D,T}\,(1 - S_\Delta) - k_{\Delta E}{}^{3\Sigma} \qquad (3)$$

$k_{\Delta E}{}^{3\Sigma}$ strongly depends on the sensitizer triplet energy. With the mean value of $E_T = 250$ kJ mol^{-1}, we derived for the investigated NDs, $k_{\Delta E}{}^{3\Sigma} = 5 \times 10^6$ s^{-1},[33] which is negligible compared with the pCT component. Thus, eq 3 simplifies for this series of NDs to $k_{CT}{}^{3\Sigma} = k_{D,T}\,(1 - S_\Delta)$.

Scheme 2 is used to discuss the kinetics of the deactivation of $O_2(^1\Delta_g)$ by the ND ground states. One singlet nCT encounter complex $^1(S_0{}^1\Delta)$ is formed with a spin-statistical weight of unity, and deactivated either by collisional electronic to vibrational energy transfer to the terminal bonds of the quencher (with rate constant k_{ev}) or by formation of a pCT exciplex, and subsequent intersystem crossing (rate constant k_{isc}), leading to the ground states.

For derivatives not bearing any electron-donating substituent, CT effects are neither expected nor observed. The overall quenching rate constant $k_\Delta{}^Q$ does not vary significantly among NAPH, 1FN, and 2BRN. Hence we estimate the e−v contribution of one aromatic C−H bond to the quenching of $O_2(^1\Delta_g)$ from the mean value of its contribution to the quenching by these three compounds to be 467, 488, and 590 M^{-1} s^{-1}, in TET, DCM, and ACN, respectively. The e−v deactivation by other terminal bonds of the NDs is negligible because of their significantly lower vibrational frequencies.[12] The increase of the incremental rate constant from TET to ACN is small, and could be caused by the increase of the collisional frequency.[13,44] In default of solvent-dependent data for the deactivation of $O_2(^1\Delta_g)$ by aliphatic C−H bonds, we will use the average value of 309 M^{-1} s^{-1}, which was derived for pure liquids.[12] Both contributions add to give the rate constant of e−v deactivation, k_{ev}. In the present work, we will only discuss the CT pathway, whose rate constant $k_\Delta{}^{3\Sigma}$ is given by eq 4,

$$k_\Delta{}^{3\Sigma} = k_{D,\Delta} - k_{ev} = \frac{k_{ex}k_{isc}}{k_{-ex} + k_{isc}} \qquad (4)$$

where $k_{D,\Delta} = k_{-diff}k_\Delta{}^Q/(k_{diff} - k_\Delta{}^Q)$. We assume for both quenching processes $k_{-diff} = gk_{diff}/\mathrm{M}^{-1}$, with $g = 1$, whereby M = mol L^{-1}, as was already done by Gijzeman et al.[20] and Wilkinson et al.[30] A larger value of g would lead to proportionnally larger values for all nCT complex deactivation rate constants, but the relative changes of $k_{D,T}$ and $k_{D,\Delta}$ would remain the same. One major difference with the T_1 deactivation process is that the decay of the $^1(S_0{}^1\Delta)$ complexes is an isc process, while $^3(T_1{}^3\Sigma)$ exciplexes decay via ic. It is unknown which step is rate determining in the deactivation of $O_2(^1\Delta_g)$. Two limiting cases are possible: (i) if $k_{isc} \gg k_{-ex}$, the CT quenching rate constant is given by $k_\Delta{}^{3\Sigma} = k_{ex}$, and (ii) when $k_{-ex} \gg k_{isc}$, we obtain $k_\Delta{}^{3\Sigma} = K_{ex}\, k_{isc}$, with $K_{ex} = k_{ex}/k_{-ex}$.

It is our objective to analyze the CT-induced processes leading via intermediates of different statistical weight to the quenching of T_1 and $O_2(^1\Delta_g)$. Since the overall rate constants of triplet state quenching of naphthalenes by O_2 are much smaller than the spin-statistical limit of $^4/_9 k_{diff}$, see Table 1, it is unlikely that the $^5(T_1{}^3\Sigma)$ quintet complex significantly contributes to its formation in this case. Therefore, we account for the 3-fold smaller statistical weight of the intermediate $^3(T_1{}^3\Sigma)$ nCT complex compared with the $^1(S_0{}^1\Delta)$ nCT complex by multiplying $k_{CT}{}^{3\Sigma}$ with the factor 3.[45] As a general designation for the rate constant of CT induced quenching, we will use k_{CT} for both $3k_{CT}{}^{3\Sigma}$ and $k_\Delta{}^{3\Sigma}$**.**

We are aiming to quantitatively distinguish quenching data from different solvents; thus, it is essential to obtain a dependable estimate of the electrostatic interaction energy C between a radical ion pair and a solvent of dielectric constant ϵ_s. According to Weller, C can be calculated from eq 5, if E_{ox} and E_{red} have been determined in acetonitrile.[46]

$$C = \frac{e^2}{2}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)\left(\frac{1}{\epsilon_s} - \frac{1}{37}\right) - \frac{e^2}{\epsilon_s(r^+ + r^-)} \qquad (5)$$

e is the elementary charge, and e^2 = 14.43 eV Å. The radius r^+ of the electron donor does not vary significantly within a series of NDs, hence we will use the representative mean value of 3.23 Å, from 3.08 Å for naphthalene and 3.37 Å for dimethylnaphthalene, to account for the whole series. r^- of the acceptor O_2 is 1.73 Å. Molecular radii have been obtained from the van der Waals volumes estimated according to Bondi,[47] assuming

TABLE 1

			DCM		TET[a]		ACN[b]	
sensitizer	E_T,[c] kJ mol^{-1}	E_{ox},[d] V vs SCE	S_Δ[e]	k_T^Q,[f] 10^9 M^{-1}s^{-1}	S_Δ[e]	k_T^Q,[f] 10^9 M^{-1}s^{-1}	S_Δ[e]	k_T^Q,[f] 10^9 M^{-1} s^{-1}
26DMEON	253	1.14[g]	0.30[h]	6.58				
1MEON	256[a]	1.26[a]	0.46	6.89	0.52	3.78	0.33	7.2
27DMEON	245	1.34[g]	0.53	4.68				
ACEN	250[a]	1.34[a]	0.58	4.57	0.59	2.84	0.41	6.5
2MEON	253[a]	1.38[a]	0.62	3.85	0.75	2.34	0.44	5.3
26DMEN	252[a]	1.49[a]	0.65	2.60	0.80	2.03		
23DMEN	247	1.50[g]	0.62	3.05				
1MEN	257[a]	1.54[a]	0.72	2.46	0.81	1.70	0.60	3.2
2MEN	253[a]	1.61[a]	0.72	2.39	0.85	1.65	0.61	3.1
NAPH	255[a]	1.65[a]	0.62	1.88	0.88	1.33	0.62	2.6
1BRN	247[a]	1.77[a]	0.83	1.25	0.98_4	1.18	0.77	1.8
2BRN	255	1.90[b]	0.76	1.53			0.68	1.8
1CNN	243[a]	2.01[a]	0.91	1.20	0.98	0.93	0.74	1.4

[a] Reference 33. [b] Reference 27. [c] ±4 kJ mol^{-1}. [d] ±0.02 V. [e] ±4%. [f] ±10%. [g] Courtesy of A. A. Abdel-Shafi and F. Wilkinson. [h] By direct irradiation at 308 nm, taking into account the triplet quantum yield of 0.95 determined by PAC.

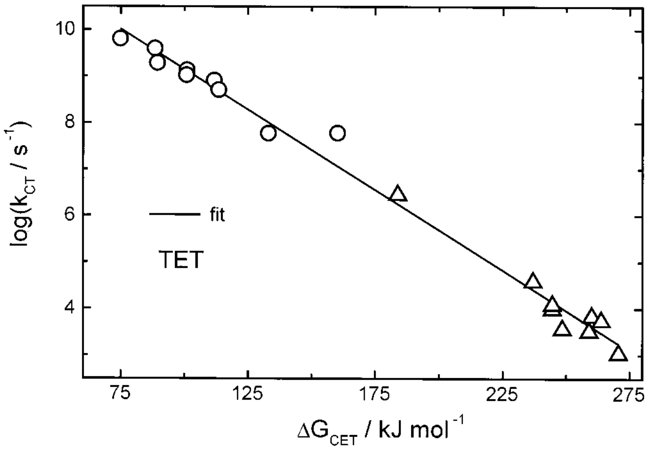


Figure 1. Linear dependence of log(k_{CT}) (in TET) on the free energy change ΔG_{CET} for a complete electron transfer to oxygen. Circles correspond to T_1, triangles to $O_2(^1\Delta_g)$ deactivation.

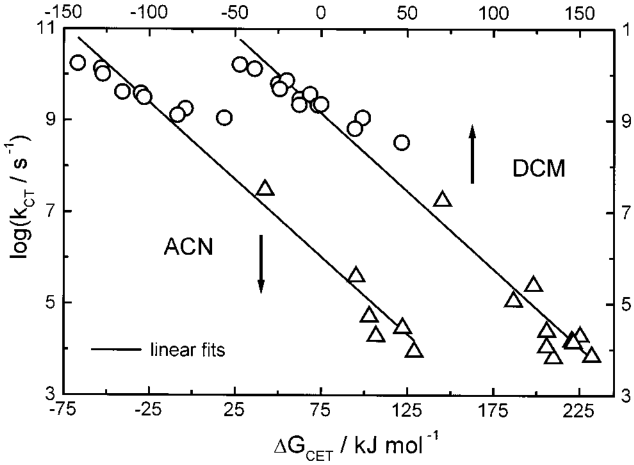


Figure 2. Linear dependence of log(k_{CT}) on ΔG_{CET} in DCM (upper scale) and ACN (lower scale). Circles correspond to T_1, triangles to $O_2(^1\Delta_g)$ deactivation.

a spherical molecular shape. Using these values, we calculate the electrostatic interaction energy to be 134, 20.4, and −7.6 kJ mol^{-1}, in TET, DCM, and ACN, respectively.

Discussion

In agreement with previous work, we find that log(k_{CT}) for both CT quenching of naphthalene triplet states by ground state oxygen and of singlet oxygen by ground state naphthalenes correlates linearly with ΔG_{CET} calculated from eqs 1 and 5, with slopes very similar to those previously obtained in different solvents. Moreover, we find that the correlation for deactivation of $O_2(^1\Delta_g)$ apparently grows into the correlation for deactivation of T_1. This is shown in Figure 1, which reveals that both excited to ground state CT quenching processes are readily described by one common linear dependence of ΔG_{CET}. This common driving-force dependence of quenching rate constants indicates for the first time that there is a common deactivation channel for the pCT complexes generated during quenching of excited triplet NDs by ground state oxygen and quenching of excited singlet oxygen by singlet ground state NDs. A common mechanism would furthermore imply that, equally to the T_1 quenching process, the rate-determining step in the CT deactivation of $O_2(^1\Delta_g)$ is the formation of the pCT complex.

According to a treatment previously used for these and other systems of photoinduced partial electron transfer, an estimate of the CT character of the exciplexes is obtained from the ratio β of the experimental slope s of log(k_{CT}) vs ΔG_{CET} to the limiting slope for complete electron transfer in the endergonic range,[18,29,31–33,48–51] which amounts to $-(2.3RT)^{-1} = -0.175$ mol kJ^{-1}, at 25 °C. Figure 1 yields $s = -0.0346$ mol kJ^{-1} in TET. The same treatment of the data leads to $s = -0.0341$ mol kJ^{-1} in DCM and $s = -0.0338$ mol kJ^{-1} in ACN, corresponding to a CT character decreasing from 19.8% in TET to 19.3% in ACN. However, at least in the polar solvents, a common linear dependence is not the only possible interpretation, see Figure 2.

The T_1 quenching data appear to deviate systematically from the correlation, and it may be argued that the common pattern in TET is due to a coincident equivalence of the ΔG_{CET} dependence of two different mechanisms, with $O_2(^1\Delta_g)$ quenching approaching the limiting case where $k_\Delta^{3\Sigma} = K_{ex}\, k_{isc}$. An individual analysis of the T_1 deactivation process yields $\beta = 15.1\%$ (TET), $\beta = 10.4\%$ (DCM), and $\beta = 8.7\%$ (ACN). Similar values have been found for a series of biphenyl derivatives by Wilkinson and Abdel-Shafi, who observed a slight decrease in β in going from cyclohexane to ACN.[30] This inverse dependence of the CT character on solvent polarity has been explained by the transition state for the CT-assisted quenching being closer in nature to the nCT complex than to the pCT exciplexes, but is still very surprising, as it contradicts the observed increase of charge-transfer character of exciplexes with increasing solvent polarity.[57] Such behavior is not observed for the $O_2(^1\Delta_g)$ quenching process, where no significant variation of the slope

TABLE 2

sensitizer	$k_{CT} = 3k_T^{3\Sigma}$, 10^9 s^{-1} ($\Delta G_{CET} - C$), kJ mol^{-1}	DCM[a]	TET[b]	ACN
26DMEON	−67.8	16.4		
1MEON	−59.2	13.3	6.31	17.2
27DMEON	−40.5	7.42		
ACEN	−45.5	6.30	3.90	13.4
2MEON	−44.6	4.83	1.92	10.1
26DMEN	−33.0	2.91	1.35	
23DMEN	−27.0	3.75		
1MEN	−33.2	2.19	1.04	4.13
2MEN	−22.4	2.13	0.81	3.90
NAPH	−20.6	2.24	0.50	3.15
1BRN	−1.0	0.66	0.059	1.29
2BRN	3.6	1.14		1.80
1CNN	26.2	0.33	0.060	1.13

[a] $k_{diff} = 4.2 \times 10^{10}$ M^{-1} s^{-1} (ref 33). [b] $k_{diff} = 2.7 \times 10^{10}$ M^{-1} s^{-1}, interpolated from the literature data of k_{diff}[30] and viscosity[59] for ACN (4.5×10^{10} M^{-1} s^{-1}, 0.360 cP), DCM (0.421 cP), and cyclohexane (2.72×10^{10} M^{-1} s^{-1}, 0.975 cP).

of log(k_{CT}) vs ΔG_{CET} is seen. This finding is not less surprising, as it should be reasonable to expect some solvent dependence of the CT enhancement, whatever the rate constants depend on k_{ex} or K_{ex}. All in all, the above discussion leaves a rather confusing and inconsistent picture for both processes, and it may be questionable whether a linear interpretation is applicable to these data, especially if one considers that ΔG_{CET} extends significantly into the exergonic range (see Table 2). A simple parabolic model, which accounts for electron-transfer reactions in a very general way, was established by Marcus.[52] This relationship describes the driving-force dependence of the activation free energy $\Delta G^\#$ of an electron transfer step, and has been most successfully applied to numerous areas, including photoinduced electron transfer, and even photoinduced partial electron transfer.[53−58] Darmanyan et al.[31] first applied Marcus theory to the deactivation of $O_2(^1\Delta_g)$ by strong electron donors. In our opinion, the partial CT nature of the process requires the introduction of a corrective coefficient f, which accounts for the fact that the effective change in free energy should be smaller than ΔG_{CET}, and equals unity in the equation derived by Marcus for complete electron-transfer processes, eq 6.

$$\Delta G^\# = \frac{\lambda}{4}\left(1 + \frac{f\,\Delta G_{CET}}{\lambda}\right)^2 \qquad (6)$$

λ is the reorganization energy. The $\Delta G^\#$ values are calculated from the data of Tables 2 and 4 using eq 7.

$$\Delta G^\# = -RT \ln\left(\frac{k_{CT}}{k_B T/h}\right) \qquad (7)$$

k_B and h are the Boltzmann and Planck constants; T is the Kelvin temperature. The dependence of $\Delta G^\#$ on ΔG_{CET} is drawn in Figure 3.

It is shown that this parabolic model describes the results more accurately than a linear interpretation. The fits describe the data rather well, with exception of the values for 1CNN, which are too low in all three solvents. This could be the consequence of a too low value of E_T, a too large value of E_{ox}, or a specific interaction between O_2 and the cyano group, replacing the interaction between O_2 and the aromatic nuclei. The solid lines are fits to eq 6, and yield $f = 0.195$ in TET, $f = 0.317$ in DCM, and $f = 0.346$ in ACN. According to eq 8, f is defined as the factor relating ΔG_{CET} to the free energy change ΔG_{CT} of pCT complex formation in the parabolic model.

TABLE 3

quencher	k_Δ^Q,[a] 10^4 M^{-1}s^{-1} DCM	TET	ACN
1DMAN	1780	280	3030
26DMEON	11.8		
1MEON	25.3	4.19	38.8
27DMEON	1.61	1.43	
ACEN	2.88	1.58	5.68
2MEON	1.09	0.78	2.44
26DMEN	2.02	0.79	
23DMEN	1.87	1.14	
1MEN	2.36	0.96	3.44
2MEN	1.15	0.53	1.39
NAPH	0.321	0.367	0.474[b]
2BRN	0.359	0.288	0.230[b]
1FN	0.385	0.371	0.595[b]

[a] Uncertainty ±7% for $k_\Delta^Q > 10^4$ M^{-1}s^{-1}, otherwise ± 10%. [b] In CD_3CN.

TABLE 4

quencher	$k_{CT} = k_\Delta^{3\Sigma}$, 10^4 s^{-1} ($\Delta G_{CET} - C$), kJ mol^{-1}	DCM	TET	ACN
1DMAN	49.8[a]	1780	280	3030
26DMEON	91.2	11.3		
1MEON	102.8	24.9	3.77	38.3
27DMEON	110.5	1.13	0.96	
ACEN	110.5	2.46	1.21	5.20
2MEON	114.4	0.660	0.36	1.93
26DMEN	125.0	1.54	0.32	
23DMEN	126.0	1.39	0.67	
1MEN	129.8	1.93	0.54	2.93
2MEN	136.6	0.72	0.11	0.88

[a] E_{ox} of 1DMAN is 0.71 V vs SCE (courtesy of A. A. Abdel-Shafi and F. Wilkinson).

TABLE 5

solvent	ϵ_{op}[a]	ϵ_s[b]	C, kJ mol^{-1}	f	λ, kJ mol^{-1}
TET	2.130	2.238[c]	134	0.195	33.6
DCM	2.03	9.08[c]	20.4	0.317	80.6
ACN	1.806	37.0[d]	−7.6	0.346	91.7

[a] Calculated from the refractive index n (ref 59), according to $\epsilon_{op} = n^2$. [b] At 20 °C. [c] Reference 39. [d] Reference 46.

$$\Delta G_{CT} = f\,\Delta G_{CET} \qquad (8)$$

We used eq 8 to calculate the abscissa of Figure 4, which shows both excited to ground-state CT quenching processes to accord with one classical Marcus relationship, as given by eq 9.

$$\Delta G^\# = \frac{\lambda}{4}\left(1 + \frac{\Delta G_{CT}}{\lambda}\right)^2 \qquad (9)$$

Both eqs 6 and 9 give the same values for the reorganization energy λ: 33.6 kJ mol^{-1} in TET, 80.6 kJ mol^{-1} in DCM, and 91.7 kJ mol^{-1} in ACN, thus increasing with increasing solvent polarity. This evolution is general to numerous electron transfer reactions, and is mainly explained by the solvent dependence of the outer reorganization energy λ_o.[53−58] Moreover, these results exhibit a noteworthy likeness with the observations of Gould et al., who calculated λ from the emission spectra of tetracyanobenzene/hexamethylbenzene exciplexes to vary from 45 kJ mol^{-1} in TET to 91 kJ mol^{-1} in dichloroethane (ϵ_s =

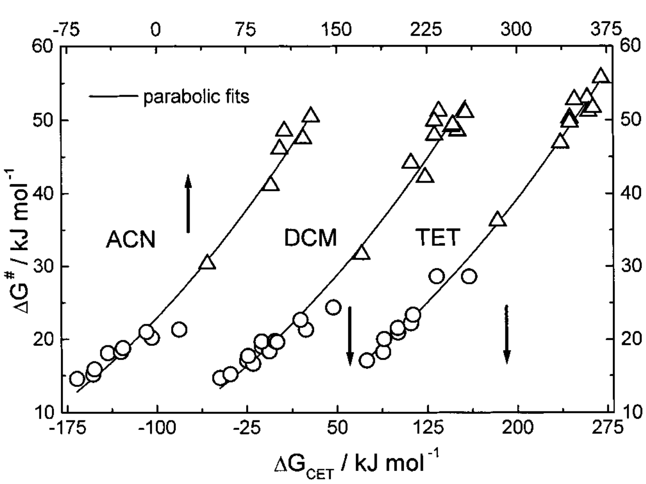


Figure 3. Parabolic dependence of $\Delta G^{\#}$ on the free energy change ΔG_{CET} for a complete electron transfer, in TET, DCM (lower scale), and ACN (upper scale). The solid lines are fits to eq 6. The resulting parameters are given in Table 5. Circles correspond to T_1, triangles to $O_2(^1\Delta_g)$ deactivation.

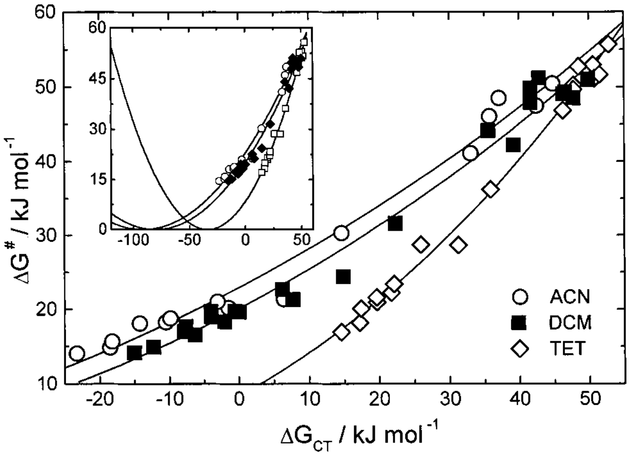


Figure 4. Parabolic dependence of $\Delta G^{\#}$ on ΔG_{CT} in three solvents. Solid lines fit to eq 9. Corresponding f and λ values are given in Table 5. The inset shows the extrapolation to the strongly exergonic region.

10.4).[58] This is also in support of a common Marcus type interpretation for our data.

Reorganization energies can be split into the sum of two independent contributions, λ_o and the inner reorganization energy λ_i, with $\lambda = \lambda_o + \lambda_i$. The former considers the solvent orientation around the reaction pair, and λ_i corresponds to the reorganization of bond lengths and inner bond angles within the reaction pair. When the reactants are considered as spheres in a dielectric continuum, we may estimate λ_o from eq 10:[53,54]

$$\lambda_o = (\delta e)^2\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right)\left(\frac{1}{2r^+} + \frac{1}{2r^-} - \frac{1}{r}\right) \qquad (10)$$

$r = r^+ + r^-$ is the inter-reactant center-to-center distance. ϵ_{op} and ϵ_s are the optical and static dielectric constants of the solvent. δ is the degree of charge transfer. Taking δ to be unity leads to λ_o values of 8 kJ mol^{-1} (TET), 129 kJ mol^{-1} (DCM), and 178 kJ mol^{-1} (ACN), thus the λ_o values for DCM and ACN are much larger than the overall reorganization energy λ calculated from eq 9, which is in accordance with the observation of an incomplete transfer of charge in the present investigation. In our first approach toward an estimation of the CT character, we will use the fact that δ can be expressed as a function of a dipole moment μ, which is defined as the product of partial charge δe and separation distance r. The CT character δ is thus given by eq 11

$$\delta = \frac{\mu}{er} \qquad (11)$$

Considering that formation of the pCT exciplex should proceed via a transition state whose dipole moment $\mu^{\#}$ does not exceed the dipole moment μ_{pCT} of the pCT complex, we may use $\mu^{\#}$ in eq 11 to evaluate the lower limit of δ. The activation free energy $\Delta G^{\#}$ can be considered to be additionnally composed of two terms, i.e., $\Delta G_{\mathrm{el}}^{\#}$, comprising all changes of free energy depending on electrostatic interaction, and an intrinsic part $\Delta G_i^{\#}$, which is assumed to be solvent independent, eq 12.

$$\Delta G^{\#} = \Delta G_{\mathrm{el}}^{\#} + \Delta G_i^{\#} \qquad (12)$$

According to a model developed by Kirkwood, the free energy of electrostatic interaction of a dipole in a spherical cavity of radius r with a continuum of dielectric constant ϵ_s is given by eq 13,[60]

$$\Delta G_{\mathrm{el}} = -\left(\frac{N_A \mu^2}{r^3}\right)q \qquad (13)$$

where N_A is the Avogadro constant, and $q = (\epsilon_s - 1)/(2\epsilon_s + 1)$. Applied to the formation of the transition state from nCT, eqs 7, 12, and 13 combine to give eq 14:

$$\ln(k_{\mathrm{CT}}) = \text{constant} + \frac{N_A}{RTr^3}(\mu^{\#2} - \mu_{\mathrm{nCT}}{}^2)q \qquad (14)$$

Hence we are able to access $\mu^{\#}$ from the slopes of linear plots of $\ln(k_{\mathrm{CT}})$ vs q, which were performed for each derivative in the three solvents. In this calculation, we used $r = 4.96$ Å, and μ_{nCT} values obtained for each ND by semiempirical calculations using AM1 parametrization.[61] μ_{nCT} varies from 0 D (NAPH) to 3.6 D (1CNN). We found no systematic increase of $\mu^{\#}$ with decreasing oxidation potential of ND, which is due to the only moderate changes in the k_{CT} data, and their corresponding experimental uncertainty. We finally arrive at mean values of $\mu^{\#} = 6.1 \pm 1.3$ D (triplet state quenching) and $\mu^{\#} = 6.2 \pm 0.8$ D (singlet oxygen quenching), corresponding to a minimum CT character $\delta = 0.25 \pm 0.05$ for both transition states. This equivalence of $\mu^{\#}$ for both processes gives one further strong indication that they proceed via the same pCT channel. Averaging over the whole series of NDs, and over the three solvents incontestably gives a rather simplistic view, but it should still yield a realistic estimate for the lower limit of the charge-transfer character of the pCT exciplexes. Using $\delta = 0.25$, we calculate λ_o from eq 10 to be 0.5 kJ mol^{-1} (TET), 8.1 kJ mol^{-1} (DCM) and 11.1 kJ mol^{-1} (ACN), which is rather low, and leads in combination with the overall reorganization energies (33.6 kJ mol^{-1} in TET, 80.6 kJ mol^{-1} in DCM, and 91.7 kJ mol^{-1} in ACN), to unrealistically large and strongly polarity dependent values for the inner reorganization energy λ_i. Hence it is reasonable to assume that the charge-transfer character of the pCT complexes is indeed larger than 25%.

In our second approach toward the estimation of the CT character, we will use the corrective factor f, which represents the effective changes in the free energy ΔG_{CT} for the formation of the exciplexes in the parabolic model. Interestingly, we observe an empirical linear correlation between f and λ, which are obtained from the fits to eqs 6 and 9, independently of each other. According to eq 10, this indicates that f may be

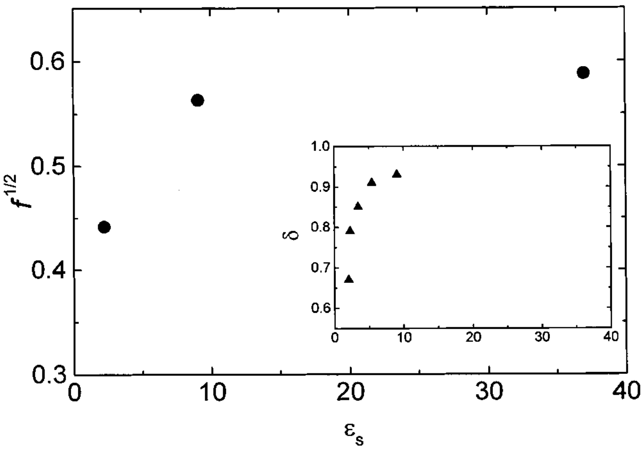
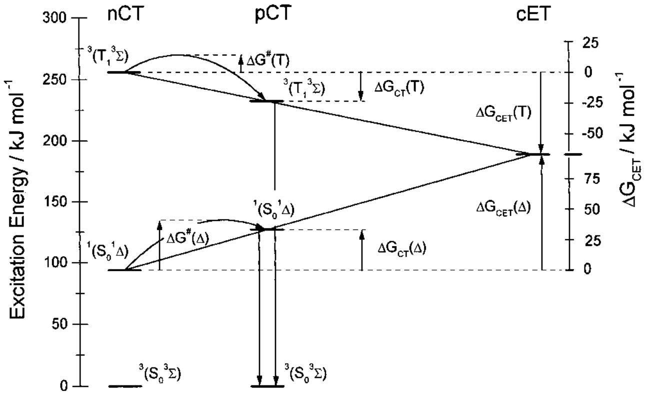


Figure 5. Dependence of $f^{1/2}$ on the static dielectric constant ϵ_s of the solvent. Inset: Dependence of δ for the 2,6,9,10-tetracyanoanthracene/*p*-xylene exciplex on ϵ_s (data taken from ref 57).

SCHEME 3



proportional to δ^2. Substituting f for δ^2 in eq 10 leads to λ_o values of 1.5 kJ mol^{-1} (TET), 40 kJ mol^{-1} (DCM), and 61.4 kJ mol^{-1} (ACN), and hence to almost solvent independent λ_i values of 32.1 kJ mol^{-1} (TET), 39.7 kJ mol^{-1} (DCM), and 30.3 kJ mol^{-1} (ACN). Moreover, the evolution of $f^{1/2}$ with the dielectric constant ϵ_s is very similar to the shape of the dependence of δ on ϵ_s seen in other systems, which demonstrate that the largest changes in δ occur in the range of $\epsilon_s < 5$ (Figure 5).[57] Thus, we believe that a relationship of the type $\delta \approx f^{1/2}$ should give realistic estimates of the CT character of sensitizer−oxygen exciplexes, and may be used as a basis for future discussions. It should be noted that any direct relationship between the charge-transfer character and the corrective factor for the driving force in the parabolic model leads to a solvent dependence that is consistent with expectations, which is one more argument in support of the common Marcus type interpretation.

Scheme 3 illustrates the results of our investigation concerning the CT induced quenching processes for the example 1MEON in ACN. The rate-determining steps lead from excited nCT complexes $^3(T_1{}^3\Sigma)$ and $^1(S_0{}^1\Delta)$ with no particular CT character, which we cannot distinguish from encounter complexes,[33] to pCT complexes $^3(T_1{}^3\Sigma)$ and $^1(S_0{}^1\Delta)$ with significant and equal CT character. The activation free energies $\Delta G^{\#}(T)$ and $\Delta G^{\#}(\Delta)$ depend via the parabolic Marcus relation (eq 9) on the corresponding free energy changes $\Delta G_{CT}(T)$ and $\Delta G_{CT}(\Delta)$. The change of free energy of the rate-determining steps is given as $\Delta G_{CT}(T) = f\Delta G_{CET}(T)$ and $\Delta G_{CT}(\Delta) = f\Delta G_{CET}(\Delta)$, whereby the corrective factor f takes the same value for both deactivation processes.

Conclusions

Quenching of singlet oxygen by ground-state naphthalene derivatives, and of naphthalene triplet states by O_2 leads to formation of partial charge transfer exciplexes whose decay exclusively yields the ground states. Both deactivation processes are described by one common dependence of the free energy change ΔG_{CT} for the formation of pCT exciplexes, which is proportional by a common factor f to the free energy change ΔG_{CET} for a complete electron transfer to oxygen, as calculated from the Rehm−Weller equation. A realistic model to fit the common dependence on ΔG_{CT} of the free energy of activation $\Delta G^{\#}$ of pCT complex formation is a parabolic Marcus type relationship. The common dependence of $\log(k_{CT})$ on ΔG_{CT} strongly indicates that there is one common deactivation channel for both processes, involving exciplexes of the same partial CT character. This is further supported by calculations of the dipole moments $\mu^{\#}$ of the transition states leading to the pCT exciplexes, which show that this parameter does not vary significantly among the two quenching processes. The corrective factor f and the reorganization energy λ, which are separately obtained from the parabolic Marcus relationship, augment noticeably with increasing solvent polarity, and appear to correlate with each other. Estimates of the outer reorganization energy λ_o, which is directly related to the degree of charge-transfer δ of the pCT exciplexes, indicate that δ is proportional to $f^{1/2}$. Although further work will be required to verify this assumption, it seems established that the CT character is larger than expected from the slopes of linear plots of $\log(k_{CT})$ vs ΔG_{CET}, and increases with increasing solvent polarity.

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