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Charge-Transfer and Non-Charge-Transfer Processes Competing in the Sensitization of Singlet Oxygen: Formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ during Oxygen Quenching of Triplet Excited Naphthalene Derivatives†

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Both excited singlet states $^1\Sigma_g^+$ and $^1\Delta_g$ and the unexcited triplet ground state $^3\Sigma_g^-$ of molecular oxygen are formed with varying rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$, respectively, during the quenching by O_2 of triplet states T_1 of sufficient energy E_T. The present paper reports these rate constants for a series of nine naphthalene sensitizers of very different oxidation potential, E_{ox} but almost constant E_T. These data complement data for $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$, determined previously for 13 sensitizers of very different E_T. The analysis of the whole set of rate constants reveals that the quenching of triplet states by O_2 results in the formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ with varying efficiencies by two different channels, each capable of producing all three product states. One quenching channel originates from excited $^{1,3}(T_1{\cdot}^3\Sigma)$ complexes without charge-transfer character (nCT), which we cannot distinguish from encounter complexes; the other originates from $^1(T_1{\cdot}^3\Sigma)$ and $^3(T_1{\cdot}^3\Sigma)$ exciplexes with partial charge-transfer character (pCT). Rate constants of formation for $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ are controlled by the respective excess energies via an energy gap relation in the nCT channel, whereas they vary with varying free energy of complete electron transfer in the pCT channel. A fast intersystem crossing equilibrium between $^1(T_1{\cdot}^3\Sigma)$ and $^3(T_1{\cdot}^3\Sigma)$ is surprisingly observed only in the nCT but not in the pCT channel.

Introduction

The quenching of excited triplet states, T_1, by molecular oxygen leads to the formation of the excited states $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ and the ground-state $O_2(^3\Sigma_g^-)$ with varying efficiencies, depending on, among other parameters, the energy of the triplet states of the organic molecules, E_T, relative to the excitation energies of $E_\Sigma = 157$ and $E_\Delta = 94$ kJ mol^{-1}.[1−7] These processes are assumed to proceed via weakly bound exciplexes $^m(T_1{\cdot}^3\Sigma)$ of multiplicity $m = 1$, 3, and 5.[8−16] Quantum yields of the sensitization of $O_2(^1\Delta_g)$ have been measured for hundreds of sensitizers.[17,18] However, despite the large number of data and numerous efforts, no clear relation has been found between the efficiency S_Δ of overall $O_2(^1\Delta_g)$ sensitization in the quenching of the T_1 state by O_2 and molecular parameters of the sensitizer such as its triplet energy E_T or its oxidation potential E_{ox}.[11,16,19−22] A major reason for this unsatisfactory situation was the missing differentiation between $O_2(^1\Delta_g)$ being directly formed with efficiency b and $O_2(^1\Delta_g)$ being indirectly formed via the very short-lived upper excited $O_2(^1\Sigma_g^+)$ which is sensitized with efficiency a.

Recently, the group of Schmidt has developed a method for the measurement of absolute values of the efficiencies of the direct formation of both $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$, a and $b = S_\Delta - a$, respectively, during the deactivation of T_1 by O_2 in CCl_4 for sensitizers with complete intersystem crossing (isc).[5] When the experimentally determined overall rate constant of T_1 quenching by O_2, k_T^Q, is at least by 1 order of magnitude smaller than the diffusion-controlled rate constant for oxygen quenching, which amounts at room temperature to $k_{diff} = 2.72 \times 10^{10}$ M^{-1} s^{-1} in CCl_4,[23,24] the rate constants of the competitive production of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ can simply be obtained as $k_T^{1\Sigma} \approx ak_T^Q$, $k_T^{1\Delta} \approx bk_T^Q$, and $k_T^{3\Sigma} \approx (1 - S_\Delta)k_T^Q$.[25] A slightly more complex evaluation has to be performed if values of k_T^Q approach the diffusion controlled limit. Then eq 1, where k_{diff} and k_{-diff} are the rate constants of formation and dissociation of weakly bound complexes $^{1,3,5}(T_1{\cdot}^3\Sigma)$, holds true if $^{1,3,5}(T_1{\cdot}^3\Sigma)$ reacts with an overall rate constant k_D to form the ground state of the sensitizer S_0 and $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, or $O_2(^3\Sigma_g^-)$ as products, respectively[13]

$$k_D = k_{-diff}k_T^Q/(k_{diff} - k_T^Q) \qquad (1)$$

It has been shown that $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ are the products of internal conversion (ic) between singlet excited complexes with subsequent dissociation, i.e., $^1(T_1{\cdot}^3\Sigma) \rightarrow {}^1(S_0{\cdot}^1\Sigma) \rightarrow S_0 + O_2(^1\Sigma_g^+)$ and $^1(T_1{\cdot}^3\Sigma) \rightarrow {}^1(S_0{\cdot}^1\Delta) \rightarrow S_0 + O_2(^1\Delta_g)$. Analogously, $O_2(^3\Sigma_g^-)$ is formed via ic from the triplet excited complex $^3(T_1{\cdot}^3\Sigma)$, yielding the triplet ground-state collision complex $^3(S_0{\cdot}^3\Sigma)$ with subsequent dissociation.[25] No direct product channel exists for $^5(T_1{\cdot}^3\Sigma)$. However, there is evidence that in some situations, $^1(T_1{\cdot}^3\Sigma)$ and $^3(T_1{\cdot}^3\Sigma)$ are populated by intersystem crossing (isc) from $^5(T_1{\cdot}^3\Sigma)$, allowing for values $k_T^Q > {}^4/_9 k_{diff}$.[14,16] For example, McLean and Rodgers demonstrated that the quenching by O_2 of the T_1 state of naphthalene in

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† Dedicated to Professor Dr. H.-D. Brauer on the occasion of his retirement.

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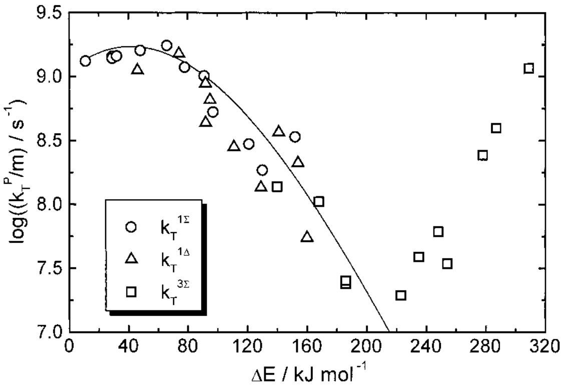

Figure 1. Dependence of $\log(k_T^P/m)$ on the excess energy ΔE of the different deactivation channels.[25,34,35] Curve describing the data is given by $9.05 + 9 \times 10^{-3}\Delta E + 1.15 \times 10^{-4}\Delta E^2 + 1.15 \times 10^{-7}\Delta E^3 + 9.1 \times 10^{-11}\Delta E^4$.

methylcyclohexane below 180 K occurs with a rate constant k_T^Q slightly larger than $^4/_9 k_{diff}$[13] and in the case of the T_1 state of p-aminoacetophenone in toluene below 220 K, $k_T^Q = 0.64k_{diff}$, i.e., distinctly larger than that spin-statistical limit.[14] Darmayan et al. have shown that for several aromatic amines in nonpolar solvents at room temperature, the values of k_T^Q are significantly larger than $^4/_9 k_{diff}$.[16] Furthermore, Grewer and Brauer found that for benzoylbiphenyl and phenalenone in the low-temperature region, where only singlet oxygen is formed, k_T^Q distinctly exceeds the corresponding spin-statistical limit of $^1/_9 k_{diff}$.[26] Therefore, no spin-statistical factors are included in eq 1. We assume somewhat abitrarily that $k_{-diff} = gk_{diff}/M$ with $g = 1$, whereby M is moles per liter, as was already done by Gijzeman.[27] A smaller value of g would lead to proportionally smaller absolute values of k_D (see eq 1). However, the relative changes of the k_D data with sensitizer would remain the same. Thus, the selection of the value of g has no influence on the present interpretation of the data. We calculate the overall rate constant for the formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ via the complexes $^{1,3,5}(T_1{\cdot}^3\Sigma)$ as $k_T^{1\Sigma} = ak_D$, $k_T^{1\Delta} = bk_D$, and $k_T^{3\Sigma} = (1 - S_\Delta)k_D$. Considering the 3-fold larger statistical weight of $^3(T_1{\cdot}^3\Sigma)$ compared with that of $^1(T_1{\cdot}^3\Sigma)$, i.e., assuming there is an equilibrium between isoenergetic singlet and triplet excited complexes, we expect $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $^1/_3 k_T^{3\Sigma}$ to be proportional to the rate constants of the respective ic processes $k_{ic}^{1\Sigma}$, $k_{ic}^{1\Delta}$, and $k_{ic}^{3\Sigma}$.[25,28]

Equation 2 was derived for the rate constant k_{ic} of a weakly bound exciplex by Kawaoka et al.[29]

$$k_{ic} = (4\pi^2/h)\rho(\Delta E)F(\Delta E)\beta^2 \tag{2}$$

Here, $\rho(\Delta E)$ is the density of final states which are nearly degenerate with the initial state, ΔE is the excess energy, $F(\Delta E)$ is the Franck−Condon factor, and β is the electronic coupling matrix element. The product $F'(\Delta E) = \rho(\Delta E)F(\Delta E)$ is the Franck−Condon weighted density of states and can be calculated from the shape of the emission spectra.[30−34] Thus, the rate constants $k_{ic}^{1\Sigma}$, $k_{ic}^{1\Delta}$, and $k_{ic}^{3\Sigma}$ and consequently $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $^1/_3 k_T^{3\Sigma}$ should depend on ΔE.

In a previous investigation, we determined values of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and k_T^3 by the simple evaluation procedure for 13 triplet sensitizers of very different triplet energy.[25,35] The more accurate evaluation via eq 1 results in only slight changes, since $k_T^Q \leq 0.1k_{-diff}$ holds true for all sensitizers with the exception of acetophenone ($k_T^Q = 4.1 \times 10^9$ M^{-1} s^{-1}).[25] Figure 1 plots newly evaluated values of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $^1/_3 k_T^{3\Sigma}$ ($= k_T^P/m$) on a logarithmic scale versus the respective excess energies $\Delta E_{1\Sigma} = E_T - E_\Sigma$, $\Delta E_{1\Delta} = E_T - E_\Delta$, and $\Delta E_{3\Sigma} = E_T$.[36]

Figure 1 demonstrates that the different rate constants depend in a common way on the excess energy for $\Delta E \leq 220$ kJ mol^{-1}. The common dependence is consistent with the assumption of an equilibrium between the singlet and triplet excited complexes $^{1,3}(T_1{\cdot}^3\Sigma)$. Furthermore, within the limits of experimental error, the corresponding matrix elements β seem to be the same.[25] Thus, the dependence of $\log(k_T^P/m)$ on ΔE, described by the empirical curve which is tentatively calculated as polynom, represents the dependence of $\log[F'(\Delta E)]$ on ΔE for the ic leading to $^1(S_0{\cdot}^1\Sigma)$, $^1(S_0{\cdot}^1\Delta)$, and $^3(S_0{\cdot}^3\Sigma)$. The Franck−Condon weighted density of states generally decreases with increasing ΔE at higher excess energies. The expression $\log[F'(\Delta E)]$ correlates with ΔE for emitting species with the steepness of the respective emission spectra in the low energy region.[30−34] However, the decline of the curve $\log(k_T^P/m)$ versus ΔE of Figure 1 is much weaker than expected from Siebrand's energy gap law, which was derived for strongly bound aromatic hydrocarbons, molecules with potential energy curves with deep minima and small anharmonicity.[30−32] Instead, the empirical curve of Figure 1 resembles much more the broad and in the low energy region rather weakly declining spectra of excimers and exciplexes when presented on corresponding scales.[33,34] We therefore concluded weakly bound excited species with shallow potential curves and large anharmonicity, i.e., weakly bound exciplex states, as the origin for ic processes leading to lower complex states and, finally, to the formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$.[25] It should be noted that the common excess energy dependence of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $^1/_3 k_T^{3\Sigma}$ illustrated by the curve of Figure 1 establishes for the first time a quantitative relation between $S_\Delta = (k_T^{1\Sigma} + k_T^{1\Delta})/(k_T^{1\Sigma} + k_T^{1\Delta} + k_T^{3\Sigma})$ and E_T.

A very different energy dependence of $^1/_3 k_T^{3\Sigma}$ with a strong and apparently linear increase of $\log(^1/_3 k_T^{3\Sigma})$ with ΔE is observed for $E_T \geq 220$ kJ mol^{-1} (see Figure 1). This change was qualitatively interpreted as resulting from a significant contribution of charge-transfer interactions between the sensitizer and O_2, which become particularly important in the high E_T region.[25] In fact, it had already been shown earlier that charge-transfer effects are important in the deactivation of T_1 states by O_2.[8−14] Quantitative relations between $k_T^{3\Sigma}$ and the free energy change ΔG_{CET} for complete electron transfer from T_1 excited sensitizer to ground-state O_2 had been found in systematic studies on two series of sensitizers of almost constant E_T but differing E_{ox} by Wilkinson et al.[19−22] and in an investigation of a larger variety of aromatic sensitizers of differing E_T and E_{ox} by Darmanyan et al.[16] ΔG_{CET} is calculated according to Rehm and Weller by eq 3,[38] where F and E_{red} are Faraday's constant and the reduction potential of the electron acceptor (for O_2, −0.78 V vs SCE)[39] and C is the electrostatic interaction energy, which is inversely proportional to the dielectric constant ϵ and is usually taken as $C = 0$ in acetonitrile

$$\Delta G_{CET} = F(E_{ox} - E_{red}) - E_T + C \tag{3}$$

A weak but still significant dependence of the overall rate constant for singlet oxygen $O_2(^1\Delta_g)$ formation on ΔG_{CET} was also noticed for sensitizers of constant E_T in the naphthalene and biphenyl series.[19−22] However, since only the sums $(k_T^{1\Sigma} + k_T^{1\Delta})$ had been determined, the actual dependences of $k_T^{1\Sigma}$ and $k_T^{1\Delta}$ on E_{ox} still remain unknown. The data of Figure 1 likewise allow no insight into the dependence of $k_T^{1\Sigma}$ and $k_T^{1\Delta}$ on ΔG_{CET}, since for most of these sensitizers no values of E_{ox} are known. Only the general dependence of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and

$k_T^{3\Sigma}$ on the respective excess energies is revealed for $\Delta E \leq 220$ kJ mol^{-1}, whereby it is unclear to what extent the scatter of the data around the curve in Figure 1 is actually caused by charge-transfer interactions between the triplet sensitizer and O_2. Furthermore, it is still an open question why charge transfer interactions should strongly affect rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ only in the $\Delta E > 220$ kJ mol^{-1} region.

It seemed very desirable to launch an investigation, particularly to clarify the role of charge-transfer interactions, on the triplet state sensitized formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ during excited-state quenching by oxygen. Therefore, we have studied the deactivation of triplet states by O_2 of naphthalene derivatives of very different oxidation potential but only slightly different triplet energy using the method for the quantitative determination of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ of sensitizers with incomplete intersystem crossing described in the preceding paper,[40] which uses indirect excitation of the sensitizer of interest. Our results allow the differentiation between two channels, both leading to $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ and only one of which originates from exciplexes with significant charge-transfer character.

Experimental Details

Acetonitrile (Aldrich, spectrophotometric grade) was dried by refluxing over calcium hydride. Tetrabutylammonium perchlorate (Fluka, >99%) was used as received. CCl_4 (Acros, 99+%, Al_2O_3), phenalenone (PHE, Aldrich, 97%, silica gel/CH_2Cl_2), 1-methoxynaphthalene (1MEON, Fluka, 98+%, Al_2O_3), and 1-bromonaphthalene (1BRN, Fluka, 97%, Al_2O_3) were purified by column chromatography. 1-Methylnaphthalene (1MEN, Aldrich, 95%) was distilled, and benzophenone (BPH, Fluka, 98+%, ethanol), acenaphthene (ACEN, Aldrich, 97%, hexane), 2-methoxynaphthalene (2MEON, Aldrich, 99%, ethanol), naphthalene (NAPH, Fluka, 98+%, pentane), and 1-cyanonaphthalene (1CNN, Aldrich, 98%, hexane) were purified by crystallization. 2,6-Dimethylnaphthalene (2,6DMEN, Aldrich, 99%), 2-methylnaphthalene (2MEN, Aldrich, 98%), erythrosin B (Aldrich, 95%), and benzene (Aldrich, 99+%) were used as supplied.

The measurement of the efficiencies a and $b = S_\Delta - a$ of the direct formation of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ in the deactivation of T_1 by O_2 of sensitizers with incomplete isc and of the rate constant k_T^Q of T_1 quenching by O_2 has been described in detail in the previous paper.[40] Four independent series of comparative experiments with reference sensitizer PHE have been performed with each sensitizer system, varying the laser pulse energy. Only energy-independent results are reported. Triplet energies have been determined by photoacoustic calorimetry (PAC) with an instrument previously described in detail.[41] BPH was also used as the primary absorber in these experiments. The naphthalene derivatives were indirectly excited by complete and fast (~1 ns) triplet−triplet energy transfer. E_T was directly obtained from the fraction of fast heat. Phosphorescence spectra have been recorded with a IF650−40 phosphoroscope from Perkin-Elmer. The half-wave oxidation potentials were measured by cyclic voltammetry in acetonitrile versus SCE, as already described.[21]

TABLE 1

sensitizer	E_{ox} (±0.02 V) vs SCE	E_T (±4 kJ mol^{-1})	$10^{-9}k_Q^T$ (M^{-1} s^{-1})^a	S_Δ^{b}	a^c
1MEON	1.26	256	3.78	0.521	0.410
ACEN	1.34	250	2.84	0.590	0.477
2MEON	1.38	253	2.34	0.750	0.635
2,6DMN	1.49	252	2.03	0.795	0.724
1MEN	1.54	257	1.70	0.808	0.705
2MEN	1.61	253	1.65	0.846	0.744
NAPH	1.65	255^d	1.33	0.880	0.802
1BRN	1.77	247	1.18	0.984	0.895
1CNN	2.01	243^e	0.93	0.979	0.850

^{a} d$x/x = \pm0.10$. ^{b} d$x/x = \pm0.04$. ^{c} d$x/x = \pm0.11$. ^{d} By PAC and phosphorescence. ^{e} By phosphorescence.

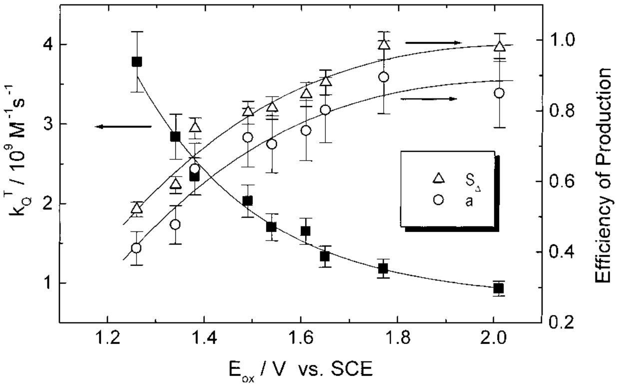

Figure 2. Effect of the sensitizer oxidation potential on the rate constant k_Q^T and the efficiencies S_Δ and a in the T_1 state quenching of naphthalene derivatives by O_2.

Results

Table 1 lists the values of E_{ox}, E_T, k_Q^T, S_Δ, and a for the nine naphthalene sensitizers investigated. The relative uncertainties dx/x of the primary data amount to ±0.10 for k_T^Q, ± 0.04 for S_Δ, and ±0.11 for a. The oxidation potentials obtained in this study differ in part significantly from the values used in earlier publications.[19,20] However, since they are all from one single source, using the same equipment, scan speeds, suppporting electrolyte, solvent, etc., the comparability should be much better compared with that for the previous E_{ox} data, which stem from different laboratories. The E_T data determined in the present study by PAC and/or phosphorescence measurements deviate only slightly from the literature data used in the previous work.[19,20]

Variation of E_{ox} causes significant variation in k_Q^T and smaller changes in S_Δ and a. Values of k_Q^T increase, whereas values of S_Δ and a decrease, with decreasing oxidation potential, see Figure 2. Interestingly, the values of the efficiency $b = S_\Delta - a$ are almost invariably an average of $b = 0.10 \pm 0.02$. The data of k_Q^T and S_Δ determined here in CCl_4 agree rather well with the corresponding data determined previously in cyclohexane.[20] We note only a significant deviation of all values of S_Δ to smaller numbers in CCl_4. The deviation, which is rather constant and amounts to −5.3 ± 1.3%, is most probably not the consequence of the change of solvent but due to using a different standard compound to measure relative singlet oxygen yields. In this work, we have used phenalenone as a standard, taking the quantum yield of singlet oxygen sensitization $Q_\Delta = 0.97$ in CCl_4[41] and obtained a maximum value $S_\Delta = 0.98$ for 1BRN. Naphthalene which was used in the previous work with cyclohexane as reference ($S_\Delta = 0.92$) led to a maximum value of $S_\Delta = 1.04$ for 1BRN.[20]

The maximum value of k_T^Q is a factor of 7 smaller than $k_{diff} = 2.72 \times 10^{10}$ M^{-1} s^{-1} in CCl_4.[23,24] We therfore calculate the overall rate constant of T_1 deactivation in the complex $^{1,3,5}(T_1{\cdot}^3\Sigma)$ using eq 1 with $k_{-diff} = k_{diff}/M$ and obtain the rate constants for the competitive formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ as $k_T^{1\Sigma} = ak_D$, $k_T^{1\Delta} = bk_D$, and $k_T^{3\Sigma} = (1 - S_\Delta)k_D$. Table 2 lists the results. From the relative errors of the primary data, we derive a constant uncertainty of d$x/x = \pm0.15$ for $k_T^{1\Sigma}$. The uncertainties of $k_T^{1\Delta}$ and $k_T^{3\Sigma}$, however, are not constant. They

TABLE 2

sensitizer	$10^{-9}k_D$ (s^{-1})[a]	$10^{-9}k_T^{1\Sigma}$ (s^{-1})[b]	$10^{-9}k_T^{1\Delta}$ (s^{-1})	dx/x	$10^{-9}k_T^{3\Sigma}$ (s^{-1})	dx/x	ΔG_{CET} (kJ mol^{-1})[c]
1MEON	4.39	1.80	0.49	0.47	2.10	0.11	−59.2
ACEN	3.17	1.51	0.36	0.54	1.30	0.12	−45.5
2MEON	2.56	1.63	0.29	0.69	0.64	0.16	−44.6
2,6DMN	2.19	1.59	0.16	1.26	0.45	0.18	−33.0
1MEN	1.81	1.28	0.19	0.85	0.35	0.20	−33.2
2MEN	1.76	1.31	0.18	0.91	0.27	0.24	−22.4
NAPH	1.40	1.12	0.11	1.27	0.17	0.31	−20.6
1BRN	1.23	1.10	0.11	1.24	0.02	2.46	−1.0
1CNN	0.96	0.81	0.12	0.82	0.02	1.87	26.2

[a] $dx/x = \pm 0.10$. [b] $dx/x = \pm 0.15$. [c] Relative scale of ΔG_{CET} values calculated with $C = 0$ by eq 3.[42]

strongly depend on the magnitude of S_Δ and a, since $k_T^{1\Delta}$ as well as $k_T^{3\Sigma}$ result in part from small differences in efficiencies. With $b = S_\Delta - a$, $dS_\Delta = 0.04S_\Delta$, and $da = 0.11a$, we derive $db/b = \{(0.04S_\Delta/(S_\Delta - a))^2 + (0.11a/(S_\Delta - a))^2\}^{0.5}$, indicating a drastic increase of the uncertainty db/b with decreasing difference $S_\Delta - a$. For the uncertainty $d(1 - S_\Delta)/(1 - S_\Delta) = 0.04S_\Delta/(1 - S_\Delta)$, a similar large uncertainty holds true when S_Δ approaches unity. Therefore, depending on the magnitude of the differences $S_\Delta - a$ and $1 - S_\Delta$, very different and particularly large relative errors may result for b and $1 - S_\Delta$ and, consequently, for $k_T^{1\Delta}$ and $k_T^{3\Sigma}$. The resulting uncertainties dx/x are separately given for each value of $k_T^{1\Delta}$ and $k_T^{3\Sigma}$ in Table 2. It does not appear to be meaningful to calculate the error limits of a definitely positive quantity x for which dx is larger than x simply as $x(1 \pm dx/x)$, since then the lower error limit would be in the negative range. Instead, we prefer to estimate the upper and lower limits by multiplying x by the factors $(1 + dx/x)$ and $1/(1 + dx/x)$, respectively. This procedure corresponds to equally positive and negative error bars on a logarithmic scale.

Discussion

A strong dependence of $k_T^{3\Sigma}$ and a weaker dependence of the sum $(k_T^{1\Sigma} + k_T^{1\Delta})$ on ΔG_{CET} was already known from the previous work of Wilkinson et al. on naphthalene derivatives.[19,20] Unknown, however, was the magnitude as well as the variation of the individual values of $k_T^{1\Sigma}$ and $k_T^{1\Delta}$ with ΔG_{CET}. Inspection of Table 2 reveals that $k_T^{1\Sigma}$ is distinctly larger than $k_T^{1\Delta}$. Furthermore, both rate constants $k_T^{1\Sigma}$ and $k_T^{1\Delta}$ increase with decreasing ΔG_{CET}. However, the variation is graduated and much weaker than for $k_T^{3\Sigma}$, and it is weakest for $k_T^{1\Sigma}$.

It is very interesting to compare these values of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ with the data measured previously for 13 different triplet sensitizers.[25] This is done best in a plot of $\log(k_T^P/m)$ versus the excess energy ΔE (see Figure 3).

Figure 3 demonstrates that charge-transfer interactions can also affect rate constants for $\Delta E < 220$ kJ mol^{-1}. Since the investigated naphthalene sensitizers have almost the same triplet energy, the data of $\log(k_T^P/m)$ for the naphthalene derivatives lie in very narrow ranges of ΔE for $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $^1/_3k_T^{3\Sigma}$. This leads for each deactivation channel to an apparently vertical increase of the values of $\log(k_T^P/m)$ with E_{ox} at almost constant ΔE.

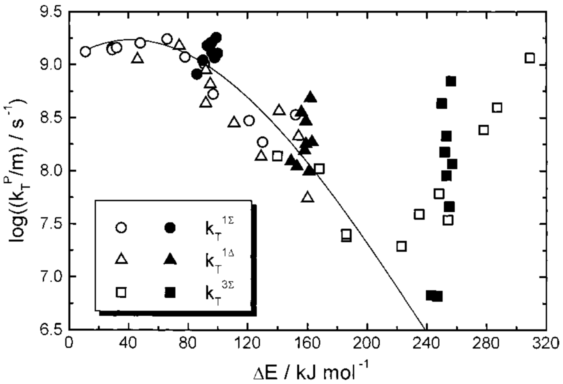

Figure 3. Dependence of $\log(k_T^P/m)$ on the excess energy ΔE of the different deactivation channels.[25,34,35] Data of the naphthalene derivatives are the filled symbols.

The smallest values of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ of the naphthalenes correspond in each case to the derivatives with the largest values of E_{ox}, for which charge-transfer interactions are minimal. Since these data are in the range of the empirical curve of Figure 3, we assume that this curve describes the excess energy dependence of rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $^1/_3k_T^{3\Sigma}$ in the absence of charge-transfer interactions. Up to now, it was assumed that weakly bound exciplexes $^{1,3}(T_1{\cdot}{}^3\Sigma)$ are the origin of this deactivation channel. However, since the curve describes the excess energy dependence for excited complexes without particular charge-transfer interactions (nCT complexes), we presume that encounter complexes $^{1,3}(T_1{\cdot}{}^3\Sigma)$ are the origin of this nCT deactivation channel. In our opinion, a meaningful differentiation between weakly bound exciplexes without charge-transfer character and excited encounter complexes is actually not possible, at least not on the basis of the known experimental results.

If the formation of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ does not proceed via exciplexes but encounter complexes, exchange energy transfer could be the operating mechanism. However, exchange energy transfer according to Dexter [43] cannot lead to such large and only moderately graduated rate constants $k_T^{1\Sigma}$ and $k_T^{1\Delta}$, since (i) the spectral overlap integrals between the broad normalized sensitizer triplet spectra and the very narrow spectra of the 0−0 transitions of the $O_2(^1\Sigma_g^+) \leftarrow O_2(^3\Sigma_g^-)$ and $O_2(^1\Delta_g) \leftarrow O_2(^3\Sigma_g^-)$ absorptions at 765 and 1275 nm are very small and (ii) the decrease of that integral in going from 765 to 1275 nm should be much stronger than the graduation of $k_T^{1\Sigma}$ and $k_T^{1\Delta}$ of about 1 order of magnitude. The spectral half width of the electronic transitions amount to only ~10 nm (765 nm)[7,44] and ~15 nm (1275 nm)[45,46] in CCl_4. Therefore, both spectral overlap integrals are approximately directly proportional to the intensities of the sensitizer emission spectra at 765 and 1275 nm, respectively. The intensity I of the fluorescence of anthracene decreases exponentially with decreasing photon energy $h\nu$. Siebrand and Williams assumed the experimental value of $d\log(I)/dh\nu = 4 \times 10^{-2}$ kJ^{-1} mol to be representative for aromatic compounds on the low energy side of the spectrum.[33] Using this slope we estimate from the difference in the respective O_2 transition energies of 61 kJ mol^{-1} a decrease of the spectral overlap integral of about 2.5 orders of magnitude. Thus, $k_T^{1\Sigma}/k_T^{1\Delta} \geq 500$ is expected in case of exchange energy transfer for each sensitizer instead of the experimentally found $k_T^{1\Sigma}/k_T^{1\Delta} \leq 10$.

The variation of $\log(k_T^P/m)$ with E_{ox} strongly increases with increasing excess energy. The vertical increase of the values of $\log(^1/_3k_T^{3\Sigma})$ of the naphthalene sensitizers at $\Delta E \approx 250$ kJ mol^{-1} demonstrates that the increase of the $\log(^1/_3k_T^{3\Sigma})$ data of the previously investigated sensitizers (open squares in Figure 3) is probably only accidentally linear at $\Delta E \geq 220$ kJ mol^{-1} and obviously a combined effect of variations in E_{ox} and E_T. The excess energy reaches maximum values for the formation of $O_2(^3\Sigma_g^-)$, since $\Delta E = E_T$. Consequently, very small values of $^1/_3k_T^{3\Sigma}$ are predicted by the empirical relation for the excess energy dependence of $\log(k_T^P/m) = f(\Delta E)$ in the absence of

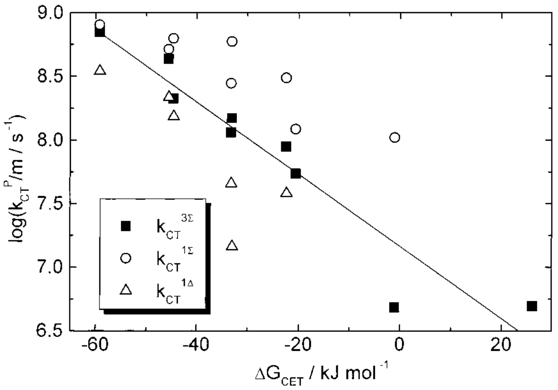

Figure 4. Dependence of $\log(k_{CT}^{P}/m)$ on the change of free energy ΔG_{CET} for complete electron transfer from T_1 to O_2.[41] Straight line with slope -0.028 kJ^{-1} mol and intercept 7.2 results from the linear fit to the $\log(^1/_3 k_{CT}^{3\Sigma})$ data.

charge-transfer interactions. This is the main reason why the effect of the variation of E_{ox} is so large for $\log(^1/_3 k_T^{3\Sigma})$. Minimum excess energies correlate, however, with the formation of $O_2(^1\Sigma_g^+)$. Correspondingly, maximum rate constants $k_T^{1\Sigma}$ are predicted by $\log(k_T^P/m) = f(\Delta E)$. Therefore the smallest effect of the variation of E_{ox} is observed for $\log(k_T^{1\Sigma})$.

Apparently, two different reaction mechanisms operate in the quenching of triplet states by O_2, both leading to the formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$. One is controlled by the variation of the excess energy, the other by the strength of charge-transfer interactions. The first occurs via excited complexes without charge-transfer character (nCT), indistinguishable from encounter complexes, the second via exciplexes with partial charge-transfer character (pCT). The corresponding rate constants are in the following, indicated by subscripts ΔE and CT, respectively. Thus, in a very simplified picture we assume eqs 4a−4c hold true

$$k_T^{1\Sigma} = k_{\Delta E}^{1\Sigma} + k_{CT}^{1\Sigma} \tag{4a}$$

$$k_T^{1\Delta} = k_{\Delta E}^{1\Delta} + k_{CT}^{1\Delta} \tag{4b}$$

$$k_T^{3\Sigma} = k_{\Delta E}^{3\Sigma} + k_{CT}^{3\Sigma} \tag{4c}$$

On this basis, we can separate the contributions of both mechanisms. The empirical curve $\log(k_T^P/m) = f(\Delta E)$ of Figure 3 is used to estimate values of $k_{\Delta E}^{1\Sigma}$, $k_{\Delta E}^{1\Delta}$, and $^1/_3 k_{\Delta E}^{3\Sigma}$. With the average triplet state energy of the naphthalene derivatives of $E_T = 250$ kJ mol^{-1} and the resulting excess energies $\Delta E_{1\Sigma} = 93$ kJ mol^{-1}, $\Delta E_{1\Delta} = 156$ kJ mol^{-1}, and $\Delta E_{3\Sigma} = E_T$, we obtain $k_{\Delta E}^{1\Sigma} = 1.0 \times 10^9$ s^{-1}, $k_{\Delta E}^{1\Delta} = 1.4 \times 10^8$ s^{-1}, and $^1/_3 k_{\Delta E}^{3\Sigma} = 1.8 \times 10^6$ s^{-1}. If these basic rate constants, which, of course, have some experimental uncertainty, are subtracted from $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $^1/_3 k_T^{3\Sigma}$, we obtain the rate constants $k_{CT}^{1\Sigma}$, $k_{CT}^{1\Delta}$, and $^1/_3 k_{CT}^{3\Sigma}$ for the charge-transfer-induced formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ in the deactivation of exciplexes $^{1,3}(T_1{\cdot}^3\Sigma)$. This procedure works rather well for $^1/_3 k_{CT}^{3\Sigma}$, since the estimate $^1/_3 k_{\Delta E}^{3\Sigma} = 1.8 \times 10^6$ s^{-1} is distinctly smaller than $^1/_3 k_T^{3\Sigma}$ for each naphthalene derivative (see Table 2). The charge-transfer effect causes a much smaller variation in the rate constants $k_T^{1\Sigma}$ and $k_T^{1\Delta}$ (see Figure 3), for which we calculate rather small differences between large numbers. Therefore, it is not surprising that the differences $k_{CT}^{1\Sigma}$ and $k_{CT}^{1\Delta}$ become even negative for some sensitizers with high oxidation potential (see Table 2), whereby these negative differences lie still within the limits of experimental uncertainty. Figure 4 displays the positive results of $k_{CT}^{1\Sigma}$ and $k_{CT}^{1\Delta}$ together with the $^1/_3 k_{CT}^{3\Sigma}$ data for all sensitizers in a plot of $\log(k_{CT}^P/m)$ vs ΔG_{CET} at constant $E_T = 250$ kJ mol^{-1}.

Deactivation by complete electron transfer quenching occurs with rate constant k_{CET} via transient contact radical ion pairs. The corresponding correlations between $\log(k_{CET}/m)$ and ΔG_{CET} are linear in the endergonic range, where $k_{CET} \ll k_{diff}$ holds true, with slope $-0.434/(RT) = -0.175$ kJ^{-1} mol.[47] The correlation between $\log(k_{CT}^{3\Sigma}/3)$ and ΔG_{CET} is also linear.[42] The least-squares fit through the $\log(k_{CT}^{3\Sigma}/3)$ data results in the straight line with slope -0.028 ± 0.003 kJ^{-1} mol and intercept 7.2 ± 0.2 shown in Figure 3. The ratio of the slope the of linear fit and $-0.434/(RT)$ amounts to $p = 0.16$. The variable p has the meaning of a corrective factor. If the data of $\log(k_{CT}^{3\Sigma}/3)$ would be plotted versus $p\Delta G_{CET}$, a linear correlation with the limiting slope $-0.434/(RT)$ would result. Therefore, $p\Delta G_{CET}$ could be interpreted as free energy ΔG_{CT} of $^3(T_1{\cdot}^3\Sigma)$ pCT complex formation from the $^3(T_1{\cdot}^3\Sigma)$ nCT complex. The ratio p is sometimes interpreted in a very simplified picture as the amount of charge-transfer in the pCT exciplex.[16,21,48−50] However, it was shown that the extent of CT character in a series of exciplexes is not constant but increases with decreasing ΔG_{CET}.[51,52] Therefore, it is clear that the 16% charge-transfer character should be regarded as best as a possible average value for the naphthalene derivatives. In any case, the increase of $\log(k_{CT}^{3\Sigma}/3)$ with decreasing ΔG_{CET} qualitatively indicates the formation of pCT exciplexes.

The fit function $f(\Delta G_{CET}) = 7.2 - 0.028\Delta G_{CET}$ for $\log(k_{CT}^{3\Sigma}/3)$ describes the corresponding experimental data rather well. The scatter of the values of $\log(k_{CT}^{1\Sigma})$ and $\log(k_{CT}^{1\Delta})$ in Figure 4 is much larger, as a consequence of the smaller effect of charge-transfer on the rate constants $k_T^{1\Sigma}$ and $k_T^{1\Delta}$. Nevertheless, these data also decrease with increasing ΔG_{CET} and are not very far apart from $f(\Delta G_{CET})$. We note that all values of $\log(k_{CT}^{1\Delta})$ are below and all values of $\log(k_{CT}^{1\Sigma})$ above the fit and consider these observations as significant. Thus, it appears as if the dependence on ΔG_{CET} could be very similar for $^1/_3 k_{CT}^{3\Sigma}$, $k_{CT}^{1\Sigma}$, and $k_{CT}^{1\Delta}$.

Competitive ic from nCT complexes $^{1,3}(T_1{\cdot}^3\Sigma)$ is the rate-determining step of the deactivation of T_1 by O_2 in the absence of charge-transfer interactions. In the presence of charge-transfer interactions, larger values of $\log(k_T^P/m)$ are observed, which are the consequence of the opening of the pCT deactivation channel. Both nCT and pCT deactivation processes contribute to the overall rate constant $k_D = k_T^{1\Sigma} + k_T^{1\Delta} + k_T^{3\Sigma}$, i.e., to the rate determining step. The verification of this model is possible by comparing calculated rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ with experimental data. Assuming that the rate constants $k_{CT}^{3\Sigma}$, $k_{CT}^{1\Sigma}$, and $k_{CT}^{1\Delta}$ vary as parallels with ΔG_{CET} in a semilogarithmic plot, we calculate fit functions for the rate constants $k_{CT}^{1\Sigma}$, $k_{CT}^{1\Delta}$, and $k_{CT}^{3\Sigma}$ by $\log(k_{CT}^{3\Sigma}) = \log(3) + f(\Delta G_{CET})$, $\log(k_{CT}^{1\Sigma}) = \log(1.5) + f(\Delta G_{CET})$, and $\log(k_{CT}^{1\Delta}) = \log(0.4) + f(\Delta G_{CET})$. Adding to the resulting fit functions $k_{CT}^{1\Sigma}$, $k_{CT}^{1\Delta}$, and $k_{CT}^{3\Sigma}$ the average rate constants of the naphthalene derivatives derived above of $k_{\Delta E}^{1\Sigma} = 1.0 \times 10^9$ s^{-1}, $k_{\Delta E}^{1\Delta} = 1.4 \times 10^8$ s^{-1}, and $k_{\Delta E}^{3\Sigma} = 5.4 \times 10^6$ s^{-1}, we finally obtain best fit functions for the rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ which describe the respective experimental data surprisingly well (see Figure 5).

It is reasonable to assume that by analogy to the deactivation of the nCT complexes the deactivation of pCT exciplexes $^{1,3}(T_1{\cdot}^3\Sigma)$ occurs by ic to lower excited pCT complexes $^1(S_0{\cdot}^1\Sigma)$, $^1(S_0{\cdot}^1\Delta)$, and $^3(S_0{\cdot}^3\Sigma)$. If the respective average excess energies of 93, 156, and 250 kJ mol^{-1} are considered, the corresponding graduation $k_{CT}^{1\Sigma} > k_{CT}^{1\Delta} > {^1/_3} k_{CT}^{3\Sigma}$ would be expected if the ic processes were the rate determining steps, as it is the case

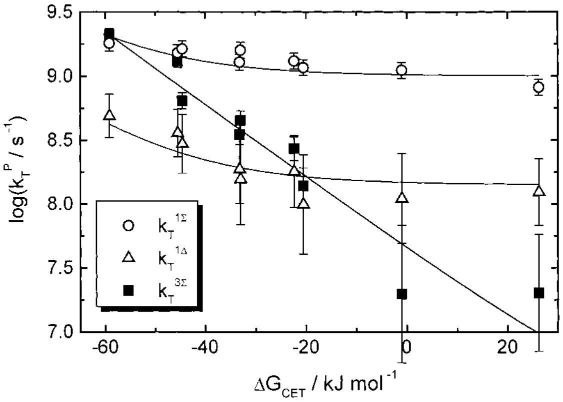

Figure 5. Dependence of $\log(k_{\mathrm{T}}{}^{1\Sigma})$, $\log(k_{\mathrm{T}}{}^{1\Delta})$, and $\log(k_{\mathrm{T}}{}^{3\Sigma})$ of the naphthalene derivatives on ΔG_{CET}. Fit functions $\log(k_{\mathrm{CT}}{}^{3\Sigma}) = \log(3) + f(\Delta G_{\mathrm{CET}})$, $\log(k_{\mathrm{CT}}1\Sigma) = \log(1.5) + f(\Delta G_{\mathrm{CET}})$, and $\log(k_{\mathrm{CT}}{}^{1\Delta}) = \log(0.4) + f(\Delta G_{\mathrm{CET}})$ with $f(\Delta G_{\mathrm{CET}}) = 7.2 - 0.028\Delta G_{\mathrm{CET}}$. For details, see text.

with the nCT complexes. The constants which are added to $f(\Delta G_{\mathrm{CET}})$ in the above derived fit functions for $\log(k_{\mathrm{CT}}{}^{3\Sigma})$, $\log(k_{\mathrm{CT}}{}^{1\Sigma})$, and $\log(k_{\mathrm{CT}}{}^{1\Delta})$ correspond to the weight factors of 3, 1.5, and 0.4 for the fit functions for $k_{\mathrm{CT}}{}^{3\Sigma}$, $k_{\mathrm{CT}}{}^{1\Sigma}$, and $k_{\mathrm{CT}}{}^{1\Delta}$. Thus, it is true, $k_{\mathrm{CT}}{}^{1\Sigma}$ is by 1.5/0.4 larger than $k_{\mathrm{CT}}{}^{1\Delta}$, consistent with the correspondingly smaller excess energy. However, $k_{\mathrm{CT}}{}^{1\Delta}$ is not larger than ${}^{1}/_{3}k_{\mathrm{CT}}{}^{3\Sigma}$ but even smaller than ${}^{1}/_{3}k_{\mathrm{CT}}{}^{3\Sigma}$. Therefore, it is not ic but the formation of the pCT exciplexes ${}^{1,3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ that is probably the slowest and, thus, the rate-determining process. Therefore, ${}^{1}/_{3}k_{\mathrm{CT}}{}^{3\Sigma}$ could still be larger than $k_{\mathrm{CT}}{}^{1\Delta}$ despite the larger excess energy. However, it is important that the graduation $k_{\mathrm{CT}}{}^{1\Sigma} \gg k_{\mathrm{CT}}{}^{1\Delta}$ is still valid, since ic from ${}^{1}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ to ${}^{1}(\mathrm{S}_0{\cdot}{}^1\Sigma)$ competes in the singlet pCT channel directly with ic to ${}^{1}(\mathrm{S}_0{\cdot}{}^1\Delta)$.

We have to assume that there exists no fast isc equilibrium between ${}^{1}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ and ${}^{3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ pCT complexes, in contrast to the situation with the nCT complexes. If a fast isc equilibrium existed, the graduation $k_{\mathrm{CT}}{}^{1\Sigma} > k_{\mathrm{CT}}{}^{1\Delta} > {}^{1}/_{3}k_{\mathrm{CT}}{}^{3\Sigma}$ according to the excess energies should again be expected, since competitive ic via the singlet and triplet pCT channels would occur. This is consistent with deactivation of ${}^{1}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ and ${}^{3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ pCT complexes by ic being much faster than isc. Since up to now it was assumed that isc between ${}^{1}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ and ${}^{3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ occurs principally as a CT induced process, i.e., between pCT complexes,[8,11,16,21,22] this is a rather surprising result.

The ${}^{1}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ and ${}^{3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ pCT exciplexes are formed from ${}^{1,3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ nCT complexes. Consequently, the statistical weight of the triplet pCT channel when compared with the singlet pCT channel should be 3. However, according to the fit results, the weight is smaller than 3. The weight factors of the fit functions $k_{\mathrm{CT}}{}^{3\Sigma}$, $k_{\mathrm{CT}}{}^{1\Sigma}$, and $k_{\mathrm{CT}}{}^{1\Delta}$ are 3, 1.5, and 0.4, yielding a value of $1.6 = 3/1.9$ as the statistical weight of the triplet pCT channel. However, the deviation from 3 is possibly just a consequence of the experimental uncertainties of the data. This is demonstrated by the curves displayed in Figure 6, which are obtained by changing the additive constants in the fit functions for $\log(k_{\mathrm{CT}}{}^{1\Sigma})$ and $\log(k_{\mathrm{CT}}{}^{1\Delta})$ from log(1.5) and log(0.4) to log(0.67) and log(0.37), respectively. This procedure enforces the statistical weight of 3 of the triplet pCT channel.

The quality of the fit to the experimental data of $\log(k_{\mathrm{T}}{}^{3\Sigma})$ is, of course, unchanged. The fit to the data of $\log(k_{\mathrm{T}}{}^{1\Delta})$ is only slightly poorer, but we note now distinct deviations of the calculated curve from the experimental data of $\log(k_{\mathrm{T}}{}^{1\Sigma})$ to lower values in the strongly exergonic range. Nevertheless the description of the $\log(k_{\mathrm{T}}{}^{1\Sigma})$ data is much better than qualitative, since (i) the mean deviation of the calculated rate constant $k_{\mathrm{T}}{}^{1\Sigma}$ amounts to only 20% and (ii) the weak increase of $\log(k_{\mathrm{T}}{}^{1\Sigma})$ is actually reproduced. Thus, we assert that the results of these investigations on the effects of variations in triplet energy and in oxidation potentials are quantitatively described.

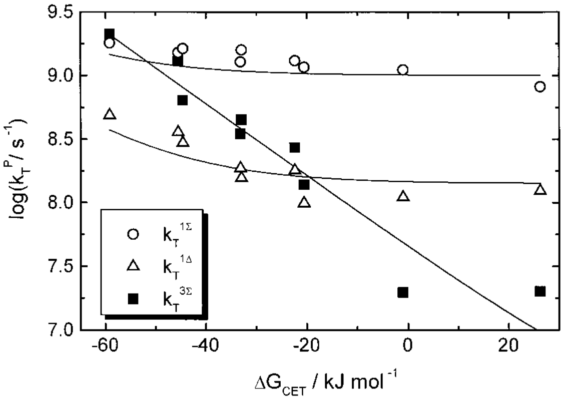

Figure 6. Dependence of $\log(k_{\mathrm{T}}{}^{1\Sigma})$, $\log(k_{\mathrm{T}}{}^{1\Delta})$, and $\log(k_{\mathrm{T}}{}^{3\Sigma})$ of the naphthalene derivatives on ΔG_{CET}. Functions: $\log(k_{\mathrm{CT}}{}^{3\Sigma}) = \log(3) + f(\Delta G_{\mathrm{CET}})$, $\log(k_{\mathrm{CT}}{}^{1\Sigma}) = \log(0.67) + f(\Delta G_{\mathrm{CET}})$, $\log(k_{\mathrm{CT}}{}^{1\Delta}) = \log(0.33) + f(\Delta G_{\mathrm{CET}})$.

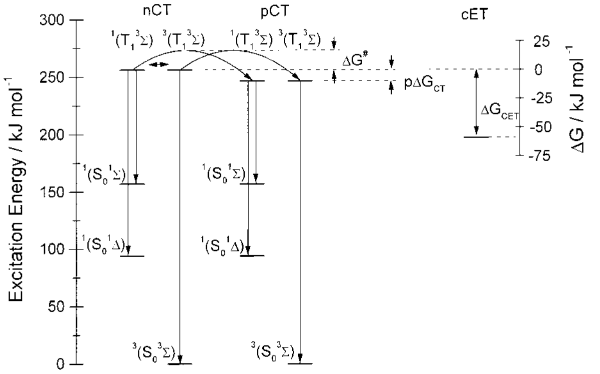

Figure 7. Schematic representation of the nCT and pCT deactivation channles. The energy scale corresponds to nCT and the free energy scale to pCT and cET. Sensitizer is 1MEON. For details, see text.

Conclusions

The results of our quantitative analysis of the $k_{\mathrm{T}}{}^{1\Sigma}$, $k_{\mathrm{T}}{}^{1\Delta}$, and $k_{\mathrm{T}}{}^{3\Sigma}$ data of 13 sensitizers of very different triplet energy and of nine sensitizers of strongly varying oxidation potential but almost constant E_{T} are summarized in Figure 7.

It is established that during oxygen quenching of triplet states the formation of $\mathrm{O}_2({}^1\Sigma_g{}^+)$, $\mathrm{O}_2({}^1\Delta_g)$, and $\mathrm{O}_2({}^3\Sigma_g{}^-)$ occurs via ic processes in two different reaction channels. One originates from ${}^{1,3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ nCT complexes i.e., without significant charge-transfer character, which we cannot distinguish from encounter complexes. The ratio of ${}^{1}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ and ${}^{3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ nCT complexes amounts to 3:1, consistently with a fast isc equilbrium following the spin-statistics. The singlet nCT complex deactivates by ic to nCT complexes ${}^{1}(\mathrm{S}_0{\cdot}{}^1\Sigma)$ and ${}^{1}(\mathrm{S}_0{\cdot}{}^1\Delta)$ and the triplet nCT complex yields ${}^{3}(\mathrm{S}_0{\cdot}{}^3\Sigma)$ by ic. These competitive ic processes are the rate-determining steps of the nCT channel. The corresponding rate constants $k_{\Delta \mathrm{E}}{}^{1\Sigma}$, $k_{\Delta \mathrm{E}}{}^{1\Delta}$, and $k_{\Delta \mathrm{E}}{}^{3\Sigma}$ are controlled by the variation of the respective excess energies following an energy gap law. The second reaction channel originates from ${}^{1,3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ pCT exciplexes, i.e., complexes with partial charge-transfer. The rate-determing step of the pCT channel is the parallel formation of the ${}^{1,3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ pCT exciplexes from ${}^{1,3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ nCT complexes, which occurs in the spin-statistical ratio 1:3. ${}^{1,3}(\mathrm{T}_1{\cdot}{}^3\Sigma)$ pCT exciplexes yield $\mathrm{O}_2({}^1\Sigma_g{}^+)$, $\mathrm{O}_2({}^1\Delta_g)$, and

$O_2(^3\Sigma_g^-)$ by ic to lower exciplex states and subsequent dissociation. Hereby, ic is much faster than isc between the $^1(T_1{\cdot}^3\Sigma)$ and $^3(T_1{\cdot}^3\Sigma)$ pCT exciplexes. Thus, we obtain the surprising result that a fast isc equilibrium between $^1(T_1{\cdot}^3\Sigma)$ and $^3(T_1{\cdot}^3\Sigma)$ exists only in the nCT but not in the pCT channel. The $^{1,3}(T_1{\cdot}^3\Sigma)$ pCT exciplexes are stabilized by charge-transfer interactions compared with the $^{1,3}(T_1{\cdot}^3\Sigma)$ nCT complexes. The corresponding change of free energy is estimated as $p\Delta G_{CET}$ where ΔG_{CET} is the change of free energy from nCT to a contact radical ion pair with complete electron transfer (cET).

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References and Notes

(1) Andrews, L. J.; Abrahamson, E. W. *Chem. Phys. Lett.* **1971**, *10*, 113.

(2) Duncan, C. K.; Kearns, D. R. *J. Chem. Phys.* **1971**, *55*, 5822.

(3) Chou, P. T.; Frei, H. *Chem. Phys. Lett.* **1985**, *122*, 87.

(4) Wang, B.; Ogilby, P. R. *J. Phys. Chem.* **1993**, *97*, 9593.

(5) Schmidt, R.; Bodesheim, M. *Chem. Phys. Lett.* **1993**, *213*, 111.

(6) Schmidt, R.; Bodesheim, M. *J. Phys. Chem.* **1994**, *98*, 2874.

(7) Chou, P.-T.; Wei, G.-T.; Lin, C. H.; Wei, C.-Y.; Chang, C.-H. *J. Am. Chem.* Soc. **1996**, *118*, 3031.

(8) Garner, A.; Wilkinson, F. *Chem. Phys. Lett.* **1977**, *45*, 432.

(9) Smith, G. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 769.

(10) Chattopadhyay, S. K.; Kumar, C. V.; Das, P. K. *J. Photochem.* **1985**, *30*, 81.

(11) Redmond, R. W.; Braslavsky, S. E. *Chem. Phys. Lett.* **1988**, *148*, 523.

(12) Darmanyan, A. P.; Foote, C. S. *J. Phys. Chem.* **1993**, *97*, 5032.

(13) McLean, A. J.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1993**, *115*, 4768.

(14) McLean, A. J.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1993**, *115*, 9874.

(15) Smith, G. *J. Am. Chem. Soc.* **1994**, *116*, 5005.

(16) Darmanyan, A. P.; Lee, W.; Jenks, W. S. *J. Phys. Chem. A* **1999**, *103*, 2705.

(17) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1993**, *22*, 113.

(18) Redmond, R. W.; Gamlin, J. N. *Photochem. Photobiol.* **1999**, *70*, 391.

(19) McGarvey, D. J.; Szekeres, P. G.; Wilkinson, F. *Chem. Phys. Lett.* **1992**, *199*, 314.

(20) Wilkinson, F.; McGarvey, D. J.; Olea, A. F. *J. Phys. Chem.* **1994**, *98*, 3762.

(21) Wilkinson, F.; Abdel-Shafi, A. A. *J. Phys. Chem. A* **1997**, *101*, 5509.

(22) Wilkinson, F.; Abdel-Shafi, A. A. *J. Phys. Chem. A* **1999**, *103*, 5425.

(23) The viscosities of cyclohexane and CCl_4 amount to 0.975 and 0.969 mPas at 20 °C.[24] Therefore we take the value $k_{diff} = 2.72 \times 10^{10}$ M^{-1} s^{-1} derived in ref 22 for cyclohexane to be also valid for CCl_4.

(24) Murov, L. S.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(25) Bodesheim, M.; Schütz, M.; Schmidt, R. *Chem. Phys. Lett.* **1994**, *221*, 7.

(26) Grewer, C.; Brauer, H.-D. *J. Phys. Chem.* **1993**, *97*, 5001.

(27) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 798.

(28) The proportionality factor is 1 if $k_{-diff} = k_{diff}/M$.

(29) Kawaoka, K.; Khan, A. U.; Kearns, D. R. *J. Chem. Phys.* **1967**, *46*, 1842.

(30) Siebrand, W.; Williams, D. F. *J. Chem. Phys.* **1967**, *46*, 403.

(31) Siebrand, W. *J. Chem. Phys.* **1967**, *47*, 2411.

(32) Siebrand, W.; Williams, D. F. *J. Chem. Phys.* **1968**, *49*, 1860.

(33) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439.

(34) Gould, I. R.; Farid, S.; Young, R. H. *Photochem. Photobiol. A: Chem.* **1992**, *65*, 133.

(35) The sensitizers are listed in with increasing triplet energy: tetraphenylporphine, 9-bromoanthracene, phenalenone, phenazine, acridine, benzanthrone, 9-fluorenone, duroquinone, 2-acetonaphthone, 4-benzoylbiphenyl, triphenylene, benzophenone, and acetophenone.

(36) The rate constants $k_T^{1\Delta}$ of the only $n\pi^*$ triplet sensitizers benzophenone and acetophenone are not shown in Figures 1 and 2. These two values are by about 1 order of magnitude larger than expected by the correlation $\log(k_T P/m) = f(\Delta E)$, indicating that the electronic configuration of T_1 ($\pi\pi^*$ or $n\pi^*$) could strongly affect the rate of $O_2(^1\Delta_g)$ formation (see refs 25 and 37).

(37) Wang, B.; Ogilby, P. R. *J. Photochem. Photobiol. A: Chem.* **1995**, *90*, 85.

(38) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(39) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(40) Shafii, F.; Schmidt, R. *J. Phys. Chem. A* **2001**, *105*, 1805.

(41) Schmidt, R.; Tanielian, C.; Dunsbach, R.; Wolff, C. *J. Photochem. Photobiol. A: Chem.* **1994**, *79*, 11.

(42) The term C is definitely positive in nonpolar solvents.[22] An estimate of $C \approx 14$ kJ mol^{-1} was given for exciplexes of O_2 and naphthalenes in cyclohexane.[20] C is expected to be much larger for complete electron transfer. Since we discuss only rate constants determined in one solvent, the relative scale of ΔG_{CET} values of Table 2 is sufficient.

(43) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

(44) Schmidt, R.; Bodesheim, M. *J. Phys. Chem.* **1995**, *99*, 15919.

(45) Schmidt, R.; Afshari, E. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 788.

(46) Wessels, J. M.; Rodgers, M. A. J. *J. Phys. Chem.* **1995**, *99*, 17586.

(47) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 835.

(48) Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1972**, *95*, 3669.

(49) Loutfy, R. O.; Dogra, S. K.; Yip, R. W. *Can. J. Chem.* **1979**, *57*, 342.

(50) Mattay, J.; Gersdorf, J.; Buchkremer, K. *Chem. Ber.* **1987**, *120*, 307.

(51) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.

(52) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8188.