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Influence of Charge Transfer Interactions on 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 Biphenyl Derivatives

Reinhard Schmidt* and Farokh Shafii

Institut für Physikalische und Theoretische Chemie, J. W. Goethe-Universität, Marie-Curie-Strasse 11, D60439 Frankfurt am Main, Germany

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Both excited singlet states $^1\Sigma_g^+$ and $^1\Delta_g$ and the 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 10 biphenyl sensitizers of very different oxidation potential, E_{ox}, but almost constant and rather large E_T. Strong and graduated charge transfer (CT) effects on $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ are observed. These data are analyzed considering data of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ determined previously for sensitizers of very different E_T and E_{ox}. The results clearly demonstrate that the quenching of triplet states by O_2 proceeds via two different channels, each capable of producing $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$. One quenching channel originates from excited $^{1,3}(T_1{\cdot}^3\Sigma)$ complexes with no CT character (nCT); the other originates from $^{1,3}(T_1{\cdot}^3\Sigma)$ exciplexes with partial charge transfer character (pCT). A common energy gap law determines the rate constants of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ formation in the nCT channel. However, the respective rate constants vary on a logarithmic scale linearly with the free energy of complete electron transfer in the pCT channel. The statistical weights of the pCT processes leading to $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ formation are 0.67, 0.33, and 3, leading to efficiencies of overall singlet and ground state oxygen formation of 0.25 and 0.75 of pCT complexes in accordance with the spin-statistical weight ratio 1:3. A fast intersystem crossing equilibrium between $^1(T_1{\cdot}^3\Sigma)$ and $^3(T_1{\cdot}^3\Sigma)$ is only observed in the nCT but not in the pCT channel.

Introduction

Photosensitized oxidations involving singlet oxygen are implicated in photodynamic inactivation of viruses and cells, in phototherapy of cancer, in photocarcinogenesis, and in photodegradation of dyes and polymers. Quenching of excited triplet states T_1 of many substances by ground state molecular oxygen O_2 produces singlet oxygen. Both lowest electronically excited singlet states $^1\Sigma_g^+$ (=$^1\Sigma$) and $^1\Delta_g$ (=$^1\Delta$) of O_2 are formed besides the $^3\Sigma_g^-$ (=$^3\Sigma$) ground state, if the T_1 state energy E_T exceeds the excitation energy $E_\Sigma = 157$ kJ mol^{-1} of the upper excited singlet oxygen species $O_2(^1\Sigma_g^+)$.[1−7] Electronical to vibrational (e−v) energy transfer deactivates $O_2(^1\Sigma_g^+)$ very rapidly and completely to the metastable and highly reactive $O_2(^1\Delta_g)$ with excitation energy $E_\Delta = 94$ kJ mol^{-1},[5,8] which is the active species in many important photoprocesses, vide supra, and which is commonly called singlet oxygen.

Quantum yields of sensitization of singlet oxygen have been measured for hundreds of sensitizers because of its outstanding importance.[9,10] It was found that the efficiency S_Δ of overall $O_2(^1\Delta_g)$ sensitization in the quenching of the T_1 state by O_2 decreases with increasing triplet energy E_T and with decreasing oxidation potential E_{ox} of the sensitizer.[11−17] Furthermore, an effect of the electronic configuration of the triplet state ($n\pi^*$ versus $\pi\pi^*$) on the magnitude of S_Δ was also noticed.[18] However, no clear relation between the values of S_Δ and these molecular parameters has been found. A major reason for this unsatisfactory situation was the missing differentiation in these studies 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*.

The situation changed when we developed methods for the measurement 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.[5] Only these methods allow the separate determination of all the three rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ of the competitive processes leading to the formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ in the quenching of T_1 states by molecular oxygen, which finally leads to a deeper insight into the complex problem.

We applied the new method of determination of these rate constants for the first time in an investigation of 13 triplet sensitizers of very different triplet state energies.[19] Plotting the values of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}/3$ 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 $\Delta E^{3\Sigma} = E_T$, we found that the rate constants of the competing processes depend in a common way on the excess energy for $\Delta E \leq 220$ kJ mol^{-1}. This at first sight surprising behavior is consistently explained. Complexes $^m(T_1{\cdot}^3\Sigma)$ of multiplicity m = 1, 3, and 5 are formed from triplet state sensitizer and $O_2(^3\Sigma_g^-)$ in the primary step.[11−26] Competitive internal conversion (ic) of the singlet excited complex $^1(T_1{\cdot}^3\Sigma)$ to lower complex states of singlet multiplicity and subsequent dissociation leads to formation of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$, 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

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* To whom correspondence should be addressed. E-mail: R.Schmidt@chemie.uni-frankfurt.de.

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the triplet excited complex $^3(T_1{\cdot}{}^3\Sigma)$, yielding the triplet ground state collision complex $^3(S_0{\cdot}{}^3\Sigma)$ which subsequently dissociates.[19] No direct product channel exists for $^5(T_1{\cdot}{}^3\Sigma)$. Assuming a spin-statistical equilibrium between isoenergetic singlet and triplet excited complexes $^1(T_1{\cdot}{}^3\Sigma)$ and $^3(T_1{\cdot}{}^3\Sigma)$, the multiplicity normalized rate constants $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}/3$ are proportional to the rate constants of the respective ic processes, which of course depend on the excess energies.[27] Thus, we discovered by a fortunate selection of sensitizers the common dependence of the rate constants $k_{ic}{}^{1\Sigma}$, $k_{ic}{}^{1\Delta}$, and $k_{ic}{}^{3\Sigma}$ on ΔE, i.e., an energy gap law for the ic processes of complexes $^{1,3}(T_1{\cdot}{}^3\Sigma)$.[19]

For $E_T \geq 220$ kJ mol^{-1} we observed an impressive complete reversion of the excess energy dependence of $k_T{}^{3\Sigma}$ and a strong increase of $\log(k_T{}^{3\Sigma}/3)$ with $\Delta E_{^3\Sigma} = E_T$. It is well-known that charge transfer (CT) interactions in complexes $^{1,3}(T_1{\cdot}{}^3\Sigma)$, which become particularly important in the high E_T region, increase with increasing values of E_T and/or decreasing oxidation potential E_{ox} leading to a decrease of S_Δ and to an increase of $k_T{}^{3\Sigma}$.[11−17,20−26] In systematic studies Wilkinson et al. demonstrated that the increase of CT interactions also leads to a significant but still weaker increase of the overall rate constant $k_T{}^{1\Sigma} + k_T{}^{1\Delta}$ of singlet oxygen formation.[11−15] Unfortunately, the influence of CT effects on the single rate constants $k_T{}^{1\Sigma}$ and $k_T{}^{1\Delta}$ could not be determined in that work.

Since rate constants $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$ depend for $T_1(\pi\pi^*)$ sensitizers of similar structure mainly on two molecular parameters, namely on E_T and E_{ox}, it is reasonable to keep one parameter constant and vary the other as was done first by Wilkinson et al.[11−14] Therefore, we recently studied the deactivation of the T_1 state by O_2 of naphthalene derivatives of very different E_{ox} but almost constant E_T.[28] This quantitative investigation revealed that the quenching of $\pi\pi^*$ 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 complexes), 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 complexes). Rate constants of formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ are controlled via an energy gap relation in the nCT channel, whereas they vary with varying free energy of complete electron transfer in the pCT channel. Furthermore, the data surprisingly indicated that a fast intersystem crossing (isc) equilibrium between $^1(T_1{\cdot}{}^3\Sigma)$ and $^3(T_1{\cdot}{}^3\Sigma)$ is established only in the nCT channel and not in the pCT channel.[28]

The conclusions of this work rest on the variation of E_{ox} at one average triplet state energy of $E_T = 250$ kJ mol^{-1}. Several such investigations at different average triplet state energies are desirable in order to quantify $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$ and thus S_Δ as functions of both variables E_T and E_{ox}. To make a further step to that goal, we investigated the deactivation of the T_1 state of biphenyl derivatives by O_2 with an average triplet energy of $E_T = 268$ kJ mol^{-1}. Since the variation of E_{ox} is very similar in both series, stronger CT interactions than in the naphthalene series could be expected.

Experimental Details

TABLE 1

sensitizer	E_{ox} ($\pm$0.02),[a] V vs SCE	E_T ($\pm$4),[a] kJ mol^{-1}	$10^{-8}k_T{}^Q$,[b] M^{-1} s^{-1}	S_Δ[c]	a[d]
DMEOB	1.30	266	114	0.347	0.248
MEOB	1.53	270	41.8	0.389	0.318
DMEB	1.69	269	23.1	0.647	0.539
MEB	1.80	272	14.6	0.730	0.610
B	1.91	274	9.81	0.721	0.623
BRB	1.95	266	8.22	0.878	0.779
CLB	1.96	269	8.70	0.854	0.744
DBRB	2.01	265	7.82	0.950	0.886
DCLB	2.02	265	7.82	0.900	0.788
CNB	2.11	265	6.42	0.942	0.838

[a] E_{ox} and E_T data from ref 13. [b] $dx/x = \pm0.10$; values of $k_T{}^Q$ for DMEOB and MEOBP have been calculated from triplet lifetimes determined with solutions which were saturated with a gas mixture of 2 vol % O_2 in N_2. [c] $dx/x = \pm0.04$. [d] $dx/x = \pm0.11$.

CCl_4 (TET, Merck, p.a., Al_2O_3), α,α,α-trifluoroacetophenone (TFAP, Aldrich, 99%, Al_2O_3), and phenalenone (PHE, Aldrich, 97%, silica gel/CH_2Cl_2) were purified by column chromatography. 4-Methoxybiphenyl (MEOB, Aldrich, 97%), 4,4′-dimethylbiphenyl (DMEB, Aldrich, 97%), 4,4′-dichlorobiphenyl (DCLB, Lancaster, 98+%), 4,4′-dibromobiphenyl (DBRB, Aldrich, 98%), and biphenyl (B, Aldrich, 99.5%) were recrystallized from ethanol. 4-Cyanobiphenyl (CNB, Aldrich, 95%) was vacuum sublimed. 4,4′-Dimethoxybiphenyl (DMEOB, Aldrich, 99%), 4-methylbiphenyl (MEB, Aldrich, 98%), 4-chlorobiphenyl (CLB, Lancaster, 99%), 4-bromobiphenyl (BLB, Aldrich, 98%), erythrosin B (Aldrich, 95%), and benzene (Aldrich, 99+%) were used as received.

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 has already been described in detail.[29] The method rests on the indirect excitation of T_1 by triplet−triplet (TT) energy transfer from an excited primary sensitizer with complete and fast isc. TFAP with $E_T = 300$ kJ mol^{-1} instead of benzophenone ($E_T = 287$ kJ mol^{-1}) was used as primary sensitizer because of the large triplet energy of the biphenyls of $E_T \leq 274$ kJ mol^{-1}.[13] We determined the triplet state lifetime of TFAP in oxygen-free CCl_4 to be 1.0 μs and in air-saturated CCl_4 to be 305 ns. Thus the T_1 state is quenched by O_2 only with efficiency $f_T{}^{O_2}(\mathrm{TFAP}) = 0.70$. Hereby, $O_2(^1\Sigma_g{}^+)$ is formed with quantum yield $Q_\Sigma = 0.24$. The overall quantum yield of $O_2(^1\Delta_g)$ sensitization by TFAP amounts to $Q_\Delta = 0.28$. The rate constants of TT energy transfer have been determined for each biphenyl derivative, and its concentration was chosen to allow for an efficiency of TT energy transfer to the secondary sensitizer in air-saturated CCl_4 of $f_T{}^{S2}(\mathrm{TFAP}) = 0.90$. Therefore, the yields of the undesired direct sensitization of $O_2(^1\Sigma_g{}^+)$ and overall sensitization of $O_2(^1\Delta_g)$ by the primary sensitizer TFAP amounted to only 0.024 and 0.028, respectively. These numbers have been used as corrections in the evaluation of the efficiencies a and $b = S_\Delta - a$ of the biphenyls.[29] Four independent series of comparative experiments with reference sensitizer PHE[30] have been performed with each sensitizer system, varying the laser pulse energy. Only energy-independent results are reported. If not otherwise noted, the experiments were carried out in air-saturated CCl_4 at 23 °C, where we calculate $[O_2] = 0.0023$ M from the oxygen concentration of 0.0124 M given for the O_2 partial pressure of 1 bar,[31] considering the CCl_4 partial pressure of 0.126 bar.[32]

Results

Table 1 lists the values of E_{ox}, E_T, the experimentally determined rate constant of T_1 quenching by O_2, $k_T{}^Q$, the efficiencies S_Δ, and a for the 10 biphenyl 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 as well as the triplet energies have been taken from Wilkinson and Abdel-Shafi.[13]

The variation of E_{ox} causes significant variation in $k_T{}^Q$ and smaller changes in S_Δ and a. Values of $k_T{}^Q$ increase, whereas values of S_Δ and a decrease with decreasing oxidation potential. Interestingly, the values of the efficiency $b = S_\Delta - a$ vary only little around an average of $b = 0.10 \pm 0.02$. Similar observations had already been made with the naphthalene sensitizers.[28] Most of the data of $k_T{}^Q$ and S_Δ determined here in CCl_4 agree rather well with the corresponding data determined previously in cyclohexane.[14] However, we note a slight but significant deviation of all values of $k_T{}^Q$ to larger numbers in CCl_4, which increases with decreasing value of E_{ox}. The maximum value $k_T{}^Q = 1.14 \times 10^{10}\ M^{-1}s^{-1}$ determined for DMEOB, for which no comparable value in cyclohexane exists, is not far from the limiting value of 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.[33]

We assume that the competitive formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ in the T_1 state quenching by O_2 involves a fast isc equilibrium between $^1(T_1{\cdot}^3\Sigma)$ and $^3(T_1{\cdot}^3\Sigma)$ nCT complexes. This approach contrasts with a kinetic scheme originally proposed by Gijzeman et al. which also considers spin statistics in the formation of $^{1,3,5}(T_1{\cdot}^3\Sigma)$ complexes but which denies a rapid isc equilibrium.[34] In that case $k_{diff}/9$ should be the upper limit of the rate constant of overall singlet oxygen formation in the quenching of T_1, as was shown by Wilkinson et al., who derived eq 1 for the probability P_1 of singlet oxygen formation in the singlet deactivation channel.[12]

$$P_1 = 9S_\Delta k_T{}^Q/k_{diff} \qquad (1)$$

P_1 is smaller than unity for all biphenyls with the exception of DMEOB, for which we calculate from the data of Table 1 $P_1 = 1.31$. This value exceeds the limiting value of 1, even if we consider an error of 25% in the estimation of k_{diff} in addition to the above given uncertainties of S_Δ, $k_T{}^Q$. Values of $P_1 > 1$ had already been found by Grewer and Brauer in low-temperature investigations with benzoylbiphenyl and phenalenone as triplet sensitizers.[35] These results strongly indicate that isc between complexes $^{1,3,5}(T_1{\cdot}^3\Sigma)$ can take place, by which the quintet complex additionally contributes to the singlet and triplet deactivation channels. Therefore, we evaluate the overall rate constant k_D of the deactivation of nCT complexes $^{1,3,5}(T_1{\cdot}^3\Sigma)$ by eq 2, assuming that these complexes are formed with rate constant k_{diff} and either dissociate back again to T_1 and $O_2(^3\Sigma_g{}^-)$ with rate constant k_{-diff} or deactivate with rate constant k_D to the products ground state sensitizer S_0 and $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, or $O_2(^3\Sigma_g{}^-)$.

$$k_D = k_{-diff}k_T{}^Q/(k_{diff} - k_T{}^Q) \qquad (2)$$

We set $k_{-diff} = gk_{diff}/M^{-1}$ with $g = 1$, whereby M is moles per liter, as was already done by Gijzeman et al.[34] A smaller value of g would lead to proportionally smaller absolute values of k_D; see eq 2. 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. With the efficiencies a and S_Δ we calculate 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 $k_T{}^{1\Sigma} = ak_D$, $k_T{}^{1\Delta} = (S_\Delta - a)k_D$, and $k_T{}^{3\Sigma} = (1 - S_\Delta)k_D$. Table 2 lists the results. A detailed consideration of the experimental uncertainties is given elsewhere.[29] From the relative errors of the primary data, we derive the uncertainties of $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$ given in Table 2. For the quantitative interpretation of the CT effect, we require values ΔG_{CET} of the change of the free energy for complete electron transfer from the triplet excited sensitizer to oxygen, which are calculated by eq 3, originally derived by Rehm and Weller.[36]

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

F and E_{red} represent Faraday's constant and the reduction potential of the electron acceptor (for O_2 −0.78 V vs SCE),[37] 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. The term C is definitely positive in nonploar solvents.[38] However, since we discuss only rate constants determined in one solvent, the relative scale of ΔG_{CET} values of Table 2 is sufficient.

TABLE 2

sensitizer	$10^{-8}k_D$,[a] s^{-1}	$10^{-8}k_T{}^{1\Sigma}$,[b] s^{-1}	$10^{-8}k_T{}^{1\Delta}$, s^{-1}	dx/x	$10^{-8}k_T{}^{3\Sigma}$, s^{-1}	dx/x	ΔG_{CET},[c] kJ mol^{-1}
DMEOB	196	48.7	19.4	0.37	128	0.18	−65.3
MEOB	49.4	15.7	3.51	0.57	30.2	0.10	−47.1
DMEB	25.2	13.6	2.73	0.63	8.91	0.12	−30.7
MEB	15.4	9.41	1.85	0.64	4.17	0.15	−23.1
B	10.2	6.34	1.00	0.84	2.84	0.14	−14.5
BRB	8.48	6.60	0.84	0.98	1.03	0.30	−2.6
CLB	8.99	6.69	0.99	0.85	1.31	0.25	−4.6
DBRB	8.05	7.13	0.52	1.70	0.40	0.77	4.2
DCLB	8.05	6.34	0.90	0.88	0.81	0.37	5.1
CNB	6.58	5.51	0.68	1.00	0.38	0.66	13.8

[a] dx/x = ±0.10; only for DMEOB dx/x = ±0.18, due to the proximity of the value of $k_T{}^Q$ to k_{diff}. [b] dx/x = ±0.15; only for DMEOB dx/x = ±0.21, due to the proximity of the value of $k_T{}^Q$ to k_{diff}. [c] Relative scale of ΔG_{CET} values calculated with $C = 0$ by eq 3.[36]

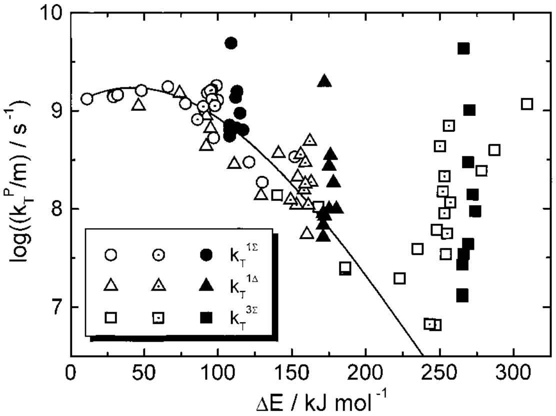


Figure 1. Dependence of $\log(k_T{}^P/m)$ on the excess energy ΔE of the different deactivation channels.[19,28] Data of the sensitizers of ref 19 as open symbols.[39,40] Data of the naphthalene derivatives as dotted symbols. Data of the biphenyl derivatives as filled symbols.

Discussion

In the primary step of the quenching process, excited complexes $^m(T_1{\cdot}^3\Sigma)$ of multiplicity $m = 1$, 3, and 5 are formed, which decay by ic to complex states of lower energy. ic processes $^1(T_1{\cdot}^3\Sigma) \rightarrow {}^1(S_0{\cdot}^1\Sigma)$ and $^1(T_1{\cdot}^3\Sigma) \rightarrow {}^1(S_0{\cdot}^1\Delta)$ lead via subsequent dissociation to the formation of $O_2(^1\Sigma_g{}^+)$ and $O_2(^1\Delta_g)$, whereas ic $^3(T_1{\cdot}^3\Sigma) \rightarrow {}^3(S_0{\cdot}^3\Sigma)$ finally yields $O_2(^3\Sigma_g{}^-)$. Assuming a spin-statistical equilibrium between isoenergetic singlet and triplet excited complexes $^1(T_1{\cdot}^3\Sigma)$ and $^3(T_1{\cdot}^3\Sigma)$, we expect $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}/3$ to be proportional to the rate constants of the ic processes $k_{ic}{}^{1\Sigma}$, $k_{ic}{}^{1\Delta}$, and $k_{ic}{}^{3\Sigma}$.[19]

Figure 1 plots the logarithms of the rate constants $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}/3$ ($=k_T{}^P/m$) versus the respective excess energies for all sensitizers including those previously investigated. The open symbols correspond to the sensitizers of our first study, which have been selected because of their complete isc and their wide range of triplet energies.[19,39−41] The symbols with dotted centers indicate the naphthalene sensitizers of the second study.[28] They have been chosen because of large variation of E_{ox} values at an average triplet energy $E_T = 250$ kJ mol^{-1}. The filled symbols belong to the biphenyl sensitizers of the present study with average $E_T = 268$ kJ mol^{-1}.

Figure 1 illustrates the excess energy dependence of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}/3$ as well as the influence of increasing CT interactions. As is shown by the open symbols, the different rate constants depend in a common way on the excess energy for $\Delta E \leq 220$ kJ mol^{-1}. This common dependence is consistent with the assumption of the competition of ic processes originating from an equilibrium between the singlet and triplet excited complexes $^{1,3}(T_1{\cdot}{}^3\Sigma)$. Kawaoka et al. derived eq 4 for the rate constant k_{ic} of a weakly bound exciplex.[42]

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

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 which decreases with increasing ΔE at higher excess energies. The rate constants of ic and consequently also $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}/3$ should depend in a common way on ΔE as long as the corresponding matrix elements β of the competing ic processes of $^1(T_1{\cdot}{}^3\Sigma)$ and $^3(T_1{\cdot}{}^3\Sigma)$ are the same, and this is actually what we have found.[19] The dependence of $\log(k_T^P/m)$ on ΔE is described by an empirical curve, which directly correlates with the dependence of $\log[F'(\Delta E)]$ on ΔE for the ic of complexes $^{1,3}(T_1{\cdot}{}^3\Sigma)$ leading to $^1(S_0{\cdot}{}^1\Sigma)$, $^1(S_0{\cdot}{}^1\Delta)$, and $^3(S_0{\cdot}{}^3\Sigma)$. The decline of this curve versus ΔE is much weaker than expected from Siebrand's energy gap law,[43−45] which was derived for strongly bound excited states, and represents an energy gap law for very weakly bound systems with no or only small binding interactions.

A very different energy dependence of $k_T^{3\Sigma}/3$ with a strong increase of $\log(k_T^{3\Sigma}/3)$ with ΔE is observed at $\Delta E_{^3\Sigma} = E_T \geq 220$ kJ mol^{-1}; see Figure 1. This change is caused by contributions of CT interactions between sensitizer and O_2 which become particularly important in the high E_T region. The influence of CT interactions is impressively demonstrated by the results obtained with the naphthalenes and even more with the biphenyls. With decreasing oxidation potential one observes at almost constant ΔE for both groups of sensitizers a graduated increase of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}/3$, which is much stronger for the biphenyl sensitizers with their larger triplet state energies. The variation of the rate constants with varying values of E_{ox} increases for the biphenyls from about 1 to 2.5 orders of magnitude in going from $k_T^{1\Sigma}$ to $k_T^{3\Sigma}/3$. Thus, a strong CT-induced quenching mechanism operates, which takes place via complexes $^{1,3}(T_1{\cdot}{}^3\Sigma)$ with partial CT character, i.e., in exciplexes.

We already noted earlier that the logarithms of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}/3$ of the naphthalene sensitizers with large E_{ox}, i.e., with small CT interactions, are near the empirical curve.[28] This also holds true for the $\log(k_T^{1\Sigma})$ and $\log(k_T^{1\Delta})$ data of the biphenyls. From this important finding we conclude that the empirical curve describes the excess energy dependence of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}/3$ for the ic of complexes $^{1,3}(T_1{\cdot}{}^3\Sigma)$ with no CT interactions (nCT complexes), which we cannot distinguish from encounter complexes. The $\log(k_T^{3\Sigma}/3)$ data of the naphthalene derivatives with large E_{ox} already lie slightly above the curve. However, for the biphenyl derivatives they start significantly above the empirical curve, due to the even larger excess energy, leading to stronger CT interactions. Thus, Figure 1 impressively illustrates that two mechanisms operate in the quenching of $\pi\pi^*$ 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 via an energy gap law by the variation of ΔE and the other by the strength of CT interactions. The first occurs via excited nCT complexes and the second via exciplexes with partial charge transfer character (pCT).

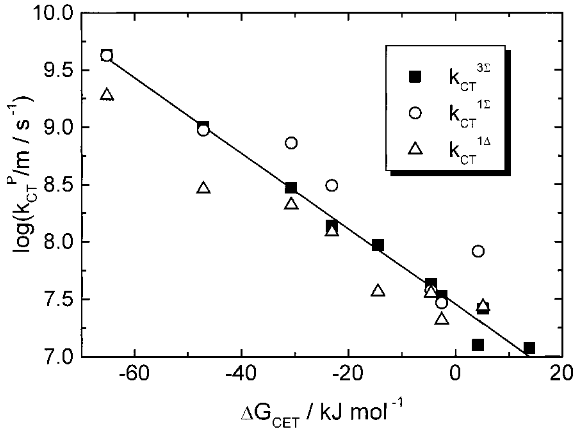


Figure 2. Dependence of $\log(k_{CT}^P/m)$ on the change of free energy ΔG_{CET} for complete electron transfer from T_1 to O_2. Straight line with slope −0.033 kJ^{-1} mol and intercept 7.45 results from the linear fit to the $\log(k_{CT}^{3\Sigma}/3)$ data.

The corresponding rate constants are in the following indicated by subscripts ΔE and CT, respectively. In a simple picture we assume eqs 5a−c hold true, which allow the separation of the contributions of both mechanisms.

$$k_T^{1\Sigma} = k_{\Delta E}^{1\Sigma} + k_{CT}^{1\Sigma} \tag{5a}$$

$$k_T^{1\Delta} = k_{\Delta E}^{1\Delta} + k_{CT}^{1\Delta} \tag{5b}$$

$$k_T^{3\Sigma} = k_{\Delta E}^{3\Sigma} + k_{CT}^{3\Sigma} \tag{5c}$$

The empirical curve $\log(k_T^P/m) = f(\Delta E)$ of Figure 1 is used to estimate values of $k_{\Delta E}^{1\Sigma}$, $k_{\Delta E}^{1\Delta}$, and $k_{\Delta E}^{3\Sigma}/3$.[46] With the average triplet state energy of the biphenyl derivatives of $E_T = 268$ kJ mol^{-1} and the resulting excess energies $\Delta E_{^1\Sigma} = 111$ kJ mol^{-1}, $\Delta E_{^1\Delta} = 174$ kJ mol^{-1}, and $\Delta E_{^3\Sigma} = E_T$, we obtain $k_{\Delta E}^{1\Sigma} = 6.3 \times 10^8$ s^{-1}, $k_{\Delta E}^{1\Delta} = 6.3 \times 10^7$ s^{-1}, and $k_{\Delta E}^{3\Sigma}/3 = 8 \times 10^5$ s^{-1}. Subtraction of these rate constants from $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}/3$ yields for each biphenyl sensitizer the rate constants $k_{CT}^{1\Sigma}$, $k_{CT}^{1\Delta}$, and $k_{CT}^{3\Sigma}/3$ (= k_{CT}^P/m) for 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 $^{1,3}(T_1{\cdot}{}^3\Sigma)$. The differences are large for the triplet, but are much smaller for the singlet channel, particularly for the sensitizers with large E_{ox} for which large uncertainties of $k_T^{1\Sigma}$ and $k_T^{1\Delta}$ result. Figure 2 displays all results of $k_{CT}^{1\Sigma}$ and $k_{CT}^{1\Delta}$ larger than 10^7 s^{-1} together with the $k_{CT}^{3\Sigma}/3$ data in a plot of $\log(k_{CT}^P/m)$ vs ΔG_{CET}.

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, with slope $-0.434/(RT) = -0.175$ kJ^{-1} mol.[47] The correlations between $\log(k_{CT}^{3\Sigma}/3)$, $\log(k_{CT}^{1\Sigma})$, and $\log(k_{CT}^{1\Delta})$ and ΔG_{CET} of Figure 2 are also linear in the rather restricted range of ΔG_{CET} values. The least-squares fit to the $\log(k_{CT}^{3\Sigma}/3)$ data, which have the smallest experimental uncertainty, results in the straight line with slope −0.033 ±

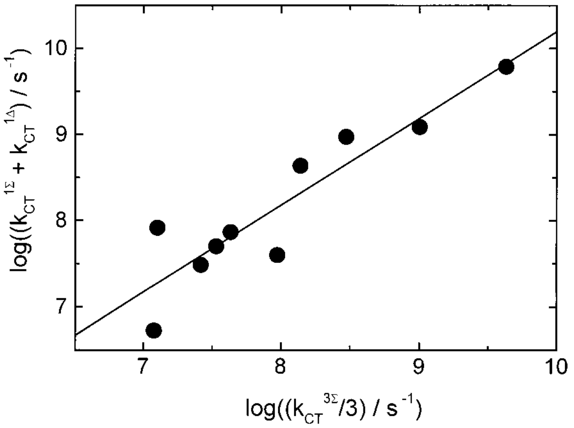


Figure 3. Correlation of $\log(k_{CT}^{1\Sigma} + k_{CT}^{1\Delta})$ with $\log(k_{CT}^{3\Sigma}/3)$. Linear least-squares fit results in slope 1.0 ± 0.1_5 and intercept 0.1 ± 0.4.

0.001 $kJ^{-1}mol$ and intercept 7.45 ± 0.10 shown in Figure 2. The ratio of the slope of the linear fit and $-0.434/(RT)$ amounts to $p = 0.19$, which is slightly larger than the corresponding ratio $p = 0.16$ obtained with the naphthalene sensitizers.[28] p is a corrective factor. If the data of $\log(k_{CT}^{3\Sigma}/3)$ was plotted versus $p\Delta G_{CET}$, a linear correlation with the limiting slope $-0.434/(RT)$ would result. Therefore, $p\Delta G_{CET}$ could have the meaning of the free energy ΔG_{CT} of $^3(T_1{\cdot}^3\Sigma)$ pCT complex formation from the $^3(T_1{\cdot}^3\Sigma)$ nCT complex in the framework of this linear free energy relationship model. The ratio p is sometimes interpreted in a very simplified picture as the fraction of charge transfer in the pCT exciplex.[13,16,48-50] However, parabolic models of the Marcus type, which can be reasonably applied to CT processes with O_2 only if a broader range of ΔG_{CET} is covered, would lead to different correction factors and to a larger and more realistic charge transfer character.[51,52] Therefore, the linear correlations of Figure 2 should quantitatively only be regarded as empirical relations describing the functional dependence between $\log(k_{CT}^{P}/m)$ and ΔG_{CET}. However, qualitatively they strongly indicate the formation of pCT exciplexes.

The fit function $f(\Delta G_{CET}) = 7.45 - 0.033\Delta G_{CET}$ describes well the experimental data of $\log(k_{CT}^{3\Sigma}/3)$. The scatter of the values of $\log(k_{CT}^{1\Sigma})$ and $\log(k_{CT}^{1\Delta})$ of Figure 2 is larger, as a consequence of the smaller CT effect on the overall rate constants $k_T^{1\Sigma}$ and $k_T^{1\Delta}$. Nevertheless, these data are not very far apart from the straight line $f(\Delta G_{CET})$. We note that most values of $\log(k_{CT}^{1\Delta})$ are below and most values of $\log(k_{CT}^{1\Sigma})$ are above the fit. It appears as if $\log(k_{CT}^{1\Sigma} + k_{CT}^{1\Delta}) \approx \log(k_{CT}^{3\Sigma}/3)$ could hold true in the series of biphenyls. This is verified in Figure 3, where we find a linear correlation of $\log(k_{CT}^{1\Sigma} + k_{CT}^{1\Delta})$ with $\log(k_{CT}^{3\Sigma}/3)$ with slope 1.0 ± 0.1_5 and intercept 0.1 ± 0.4, indicating the ratio 3:1 between the triplet and singlet pCT deactivation channels, which exactly matches the spin-statistical ratio.

This result is very important. The plot $\log(k_{CT}^{P}/m)$ versus ΔG_{CET} is much more scattered for the naphthalenes because of the significantly smaller CT effect within this series of sensitizers compared with the biphenyls;[28] see also Figure 1. Therefore, the spin-statistcal ratio 3:1 between triplet and singlet pCT deactivation channels which was used in the previous analysis of the naphthalene data was no finding but had to be assumed. Now this ratio is an unequivocal experimental result.

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 CT interactions. Larger values of $\log(k_T^{P}/m)$ are only observed as a 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 of the T_1 state quenching by O_2. This model can be verified by comparing calculated rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ with experimental data. Figures 2 and 3 tell us that $\log(k_{CT}^{3\Sigma}/3)$, $\log(k_{CT}^{1\Sigma})$, and $\log(k_{CT}^{1\Delta})$ vary with ΔG_{CET} in a very similar way. Keeping the spin-statistical ratio 3:1, we derive fit functions for $k_{CT}^{1\Sigma}$, $k_{CT}^{1\Delta}$, and $k_{CT}^{3\Sigma}$ by $\log(k_{CT}^{3\Sigma}) = \log(3) + f(\Delta G_{CET})$, $\log(k_{CT}^{1\Sigma}) = \log(x) + f(\Delta G_{CET})$, and $\log(k_{CT}^{1\Delta}) = \log(1 - x) + f(\Delta G_{CET})$ with $x < 1$. Adding to the average nCT rate constants of the biphenyls $k_{\Delta E}^{1\Sigma} = 6.3 \times 10^8$ s^{-1}, $k_{\Delta E}^{1\Delta} = 6.3 \times 10^7$ s^{-1}, and $k_{\Delta E}^{3\Sigma} = 2.4 \times 10^6$ s^{-1} the above derived pCT fit functions for $k_{CT}^{1\Sigma}$, $k_{CT}^{1\Delta}$, and $k_{CT}^{3\Sigma}$, we finally obtain the fit functions for the overall rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$. Using the value $x = 0.67$, the calculated functions describe the dependence of the respective experimental data on ΔG_{CET} surprisingly well (see Figure 4) much better than in the case of the naphthalene derivatives, where the CT effect was significantly weaker. The statistical weights of the pCT channels leading to $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ formation are $x = 0.67$ and $1 - x = 0.33$. The same values had already been used for the naphthalenes, but with less certainty. The ratio of both weights could well depend on the triplet energy of the sensitizer. However, the difference of the average values of E_T of naphthalenes and biphenyls is probably too small, and the uncertainty of the experimental data of the pCT channel of the naphthalenes too large, to see such effects.

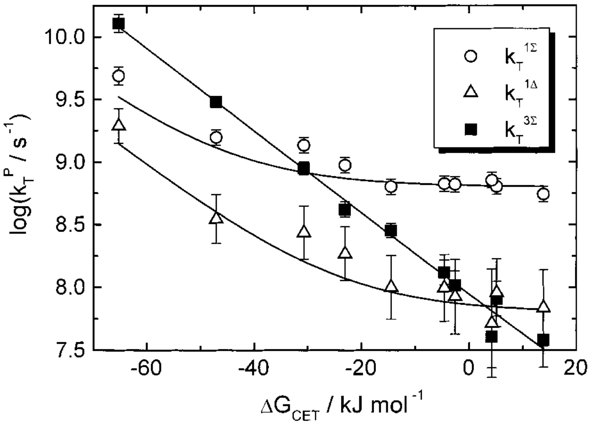


Figure 4. Dependence of $\log(k_T^{1\Sigma})$, $\log(k_T^{1\Delta})$, and $\log(k_T^{3\Sigma})$ of the biphenyl derivatives on ΔG_{CET}. Fit functions $\log(k_{CT}^{3\Sigma}) = \log(3) + f(\Delta G_{CET})$, $\log(k_{CT}^{1\Sigma}) = \log(0.67) + f(\Delta G_{CET})$, and $\log(k_{CT}^{1\Delta}) = \log(0.33) + f(\Delta G_{CET})$, with $f(\Delta G_{CET}) = 7.45 - 0.033\Delta G_{CET}$. For details see text.

It is reasonable to assume that by analogy to the deactivation of the nCT complexes an energy gap law also governs the ic of pCT exciplexes $^{1,3}(T_1{\cdot}^3\Sigma)$ to pCT complexes $^1(S_0{\cdot}^1\Sigma)$, $^1(S_0{\cdot}^1\Delta)$, and $^3(S_0{\cdot}^3\Sigma)$. Considering the respective average excess energies of 111, 174, and 268 kJ mol^{-1}, the graduation $k_{CT}^{1\Sigma} > k_{CT}^{1\Delta} > k_{CT}^{3\Sigma}/3$ is expected, if the ic processes were the rate-determining steps, as is the case with the nCT complexes. The constants which are added to $f(\Delta G_{CET})$ in the above derived fit functions for $\log(k_{CT}^{3\Sigma})$, $\log(k_{CT}^{1\Sigma})$, and $\log(k_{CT}^{1\Delta})$ correspond to the weight factors of 3, 0.67, and 0.33 for the fit functions for $k_{CT}^{3\Sigma}$, $k_{CT}^{1\Sigma}$, and $k_{CT}^{1\Delta}$. Thus, it is true that $k_{CT}^{1\Sigma}$ is by a factor of 2 larger than $k_{CT}^{1\Delta}$, which is consistent with the correspondingly smaller excess energy. However, $k_{CT}^{3\Sigma}/3$ is not smaller but by factors of 1.5 and even 3 larger than $k_{CT}^{1\Sigma}$ and $k_{CT}^{1\Delta}$ despite its largest energy gap for ic. Therefore, we must conclude that not ic but the formation of exciplexes $^{1,3}(T_1{\cdot}^3\Sigma)$ from nCT complexes $^{1,3}(T_1{\cdot}^3\Sigma)$ is the slowest and thus rate-determining process. Then $k_{CT}^{3\Sigma}/3$ could still be larger than $k_{CT}^{1\Delta}$ despite the larger excess energy. However, it is important that the graduation $k_{CT}^{1\Sigma} >$

$k_{CT}{}^{1\Delta}$ is still valid, since ic from $^1(T_1{\cdot}{}^3\Sigma)$ to $^1(S_0{\cdot}{}^1\Sigma)$ competes in the singlet pCT channel directly with ic to $^1(S_0{\cdot}{}^1\Delta)$.

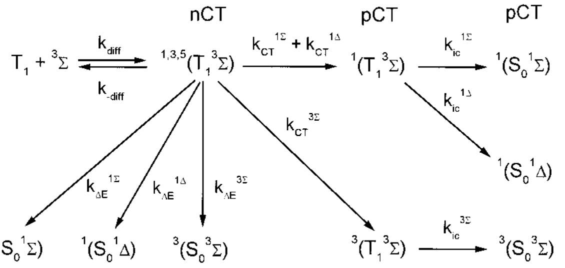
Furthermore, we have to assume that there exists no fast isc equilibrium between $^1(T_1{\cdot}{}^3\Sigma)$ and $^3(T_1{\cdot}{}^3\Sigma)$ pCT complexes, in contrast to the situation with the nCT complexes. If a fast isc equilibrium exists, the graduation $k_{CT}{}^{1\Sigma} > k_{CT}{}^{1\Delta} > k_{CT}{}^{3\Sigma}/3$ according to the excess energies should be found, since competitive ic via the singlet and triplet pCT channels would occur. Therefore, ic of pCT complexes $^1(T_1{\cdot}{}^3\Sigma)$ and $^3(T_1{\cdot}{}^3\Sigma)$ must be much faster than isc. Up to now it was mostly assumed that isc between $^1(T_1{\cdot}{}^3\Sigma)$ and $^3(T_1{\cdot}{}^3\Sigma)$ occurs principally as a CT-induced process, i.e., between pCT complexes.[13−16,20] Both conclusions had already been drawn for the naphthalene sensitizers.[28] However, the present data have much more significance than the earlier with respect to CT interactions. Therefore, the analysis of the results of this study represent a convincing confirmation of the earlier conclusions, but again it rests on the assumption that the ic in the singlet and triplet pCT channels is governed by energy gap relations.

The $^1(T_1{\cdot}{}^3\Sigma)$ and $^3(T_1{\cdot}{}^3\Sigma)$ pCT exciplexes are formed in a parallel way from $^{1,3}(T_1{\cdot}{}^3\Sigma)$ nCT complexes, which are assumed to be in a fully established spin-statistical equilibrium. Consequently, the statistical weight of the triplet pCT channel when compared with the singlet pCT channel should be 3. That is what we actually found experimentally; see Figure 3. Thus, a completely consistent picture is obtained.

If these results are of general value, one could expect the lower limiting value of $S_\Delta = 0.25$ for photochemically stable $T_1(\pi\pi^*)$ sensitizers. This limit should be reached in the case of very strong CT interactions between O_2 and triplet state sensitizer, when the formation of $^{1,3}(T_1{\cdot}{}^3\Sigma)$ pCT complexes is much faster than the ic of the corresponding nCT complexes. The upper limiting value $S_\Delta = 1$ is approached with $T_1(\pi\pi^*)$ sensitizers without significant CT interactions and with $E_T \geq 180$ kJ mol^{-1}. In this case the values of $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}/3$ are determined by the energy gap law for the ic of $^{1,3}(T_1{\cdot}{}^3\Sigma)$ nCT complexes, leading to the inequality $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta} \gg k_T{}^{3\Sigma}/3$; see Figure 1.

Our investigations on the competitive formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ are restricted to perhalogenated solvents, since only these allow the long lifetimes sufficient for the quantitative detection of $O_2(^3\Sigma_g{}^-)$. However, it is of course interesting to know how the competitive deactivation processes could be influenced on changing the solvent. We found that two mechanisms, the nCT and pCT deactivation, operate. It can reasonably be assumed that for a given sensitizer the rate constants of the pCT channel increase with solvent polarity whereas those of the nCT channel should remain practically constant. Then we expect for $T_1(\pi\pi^*)$ sensitizers with negligibly small CT interactions ($E_{ox} \geq 1.9$ V versus SCE, $250 \geq E_T \geq 180$ kJ mol^{-1}) solvent-independent values of $k_T{}^P = k_{\Delta E}{}^P$, $k_T{}^Q$, and $S_\Delta \approx 1$. Actually, we determined for the $T_1(\pi\pi^*)$ sensitizer phenalenone ($E_T = 186$ kJ mol^{-1}) the practically constant efficiency $1 \geq S_\Delta \geq 0.94$ in 13 solvents of very different polarity, including also TET and H_2O.[30] With increasing CT interactions the pCT channel becomes already effective in nonpolar solvents, leading to large values of $k_{CT}{}^P$. The increase of the solvent polarity leads for these $T_1(\pi\pi^*)$ sensitizers to further increasing rate constants $k_{CT}{}^P$ and thus $k_T{}^Q$ and as a consequence to values of S_Δ approaching the limit of 0.25. These trends can be beautifully seen in the solvent polarity dependent studies of Wilkinson et al. with the naphthalene and biphenyl $T_1(\pi\pi^*)$ sensitizers.[12,14]

SCHEME 1



Conclusions

The results of our quantitative analysis are summarized in Scheme 1.

The triplet sensitization of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ occurs via ic processes in two different reaction channels. First, $^{1,3}(T_1{\cdot}{}^3\Sigma)$ nCT complexes, i.e., encounter complexes without significant charge transfer character, are produced. The ratio of singlet to triplet $(T_1{\cdot}{}^3\Sigma)$ nCT complexes amounts to 1:3, consistent with a fast isc equilbrium dominated by the spin statistics. The ic of $^{1,3}(T_1{\cdot}{}^3\Sigma)$ nCT complexes leads to formation of ground state sensitizer and $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$. The corresponding rate constants $k_{\Delta E}{}^{1\Sigma}$, $k_{\Delta E}{}^{1\Delta}$, and $k_{\Delta E}{}^{3\Sigma}$ are controlled by the respective excess energies and follow a common energy gap law. These competitive ic processes are the rate-determining steps of the nCT channel. With increasing triplet energy and/or decreasing oxidation potential, CT interactions open the reaction path to $^{1,3}(T_1{\cdot}{}^3\Sigma)$ pCT complexes with partial charge transfer, i.e., to exciplexes. The rate-determining step of the pCT channel is the parallel formation of the $^{1,3}(T_1{\cdot}{}^3\Sigma)$ pCT exciplexes from $^{1,3}(T_1{\cdot}{}^3\Sigma)$ nCT complexes, which occurs in the spin-statistical ratio 1:3. The exciplexes yield $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ by ic to lower pCT complex states and subsequent dissociation with corresponding statistical weights of 0.67, 0.33, and 3, leading to efficiencies of overall singlet and ground state oxygen formation of 0.25 and 0.75 in the pCT channel. Hereby, ic is much faster than isc between the $^1(T_1{\cdot}{}^3\Sigma)$ and $^3(T_1{\cdot}{}^3\Sigma)$ pCT exciplexes. 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 channel.

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(40) The rate constants $k_T^{1\Delta}$ of the only nπ^* triplet sensitizers benzophenone and acetophenone are not shown in Figure 1. 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 nπ^*) could strongly affect the rate of $O_2(^1\Delta_g)$ formation; see refs 19 and 41.

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