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The Effect of Solvent Polarity on the Balance between Charge Transfer and Non-Charge Transfer Pathways in the Sensitization of Singlet Oxygen by $\pi\pi^*$ Triplet States

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A large set of literature kinetic data on triplet (T_1) sensitization of singlet oxygen by two series of biphenyl and naphthalene sensitizers in solvents of strongly different polarity has been analyzed. The rate constants and the efficiencies of singlet oxygen formation are quantitatively reproduced by a model that assumes the competition of a noncharge transfer (nCT) and a CT deactivation channel. nCT deactivation occurs from a fully established spin-statistical equilibrium of $^1(T_1{}^3\Sigma)$ and $^3(T_1{}^3\Sigma)$ encounter complexes by internal conversion (IC) to lower excited complexes that dissociate to yield $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$. IC of $^{1,3}(T_1{}^3\Sigma)$ encounter complexes is controlled by an energy gap law that is generally valid for the transfer of electronic energy to and from O_2. $^{1,3}(T_1{}^3\Sigma)$ nCT complexes form in competition to IC $^1(T_1{}^3\Sigma)$ and $^3(T_1{}^3\Sigma)$ exciplexes if CT interactions between T_1 and O_2 are important. The rate constants of exciplex formation depend via a Marcus type parabolic model on the corresponding free energy change ΔG_{CT}, which varies with sensitizer triplet energy, oxidation potential, and solvent polarity. $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ are formed in the product ratio (1/6):(1/12):(3/4) in the CT deactivation channel. The balance between nCT and CT deactivation is described by the relative contribution p_{CT} of CT induced deactivation calculated for a sensitizer of known triplet energy from its quenching rate constant. It is shown how the change of p_{CT} influences the quenching rate constant and the efficiency of singlet oxygen formation in both series of sensitizers. p_{CT} is sensitive to differences of solvent polarity and varies for the biphenyls and the naphthalenes as sigmoidal with ΔG_{CT}. This quantitative model represents a realistic and general mechanism for the quenching of $\pi\pi^*$ triplet states by O_2, surpassing previous advanced models.

Introduction

$O_2(^1\Delta_g)$ is a very reactive and highly cytotoxic species that induces photodegradation processes and has significant applications in organic synthesis and in photodynamic therapy.[1] The easiest and, in fact, most important way of $O_2(^1\Delta_g)$ production is photosensitization via excited triplet (T_1) states. Both lowest excited singlet states, $^1\Sigma_g{}^+$ and $^1\Delta_g$, of O_2 of respective energies $E_\Sigma = 157$ kJ mol^{-1} and $E_\Delta = 94$ kJ mol^{-1} are competitively formed with respective efficiencies a and b if the T_1 state energy E_T exceeds E_Σ. The upper excited $O_2(^1\Sigma_g{}^+)$ is very rapidly and completely deactivated in solution to the long-lived $O_2(^1\Delta_g)$,[2,3] which is commonly referred to as singlet oxygen. Thus, $O_2(^1\Delta_g)$ is sensitized during the O_2 quenching of T_1 states with overall efficiency $S_\Delta = a + b$.

The search for quantitative relations between physical properties of a sensitizer and both the quenching rate constant $k_T{}^Q$ and the overall efficiency S_Δ lasts already over several decades.[1] Gijzeman et al. first noted a systematic decrease of $k_T{}^Q$ for sensitizers with increasing E_T.[4] These results were complemented by Wilkinson and co-workers, who found that charge transfer (CT) interactions between T_1 excited sensitizer and O_2 lead to a strong increase of $k_T{}^Q$ in the region of high triplet energies.[5,6] Further systematic studies of the Wilkinson group revealed that increasing CT interactions lead generally to a strong increase of $k_T{}^Q$ and to a decrease of S_Δ.[6−14] These important findings have been corroborated by Cebul et al.,[15] Smith,[16] the Brauer group,[17,18] Darmanyan et al.,[19] and Abdel-Shafi and Worrall.[20] Furthermore, it was found that a CT and a non-CT (nCT) pathway compete in the quenching of triplet states by O_2 and both yield $O_2(^1\Delta_g)$ with different efficiencies.[8−14]

However, despite the large number of data and numerous efforts, no clear relations have been found between $k_T{}^Q$ and S_Δ and the molecular properties of the sensitizer. The major reason for this unsatisfactory situation was the missing differentiation between $O_2(^1\Sigma_g{}^+)$ and $O_2(^1\Delta_g)$ formed in the photosensitization process. Only the development of spectroscopic methods for the time-resolved observation of $O_2(^1\Sigma_g{}^+)$ allowed the determination of the efficiencies a and $b = (S_\Delta - a)$,[2,21,22] which are required for the evaluation of the single rate constants $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$ of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ production. T_1-excited sensitizer and $O_2(^3\Sigma_g{}^-)$ form in the primary step of quenching excited encounter $^m(T_1{}^3\Sigma)$ complexes with multiplicities $m = 1$, 3, and 5 with diffusion-controlled rate constant k_{diff}.

$$T_1 + {}^3\Sigma \underset{k_{-diff}}{\overset{k_{diff}}{\rightleftharpoons}} {}^{1,3,5}(T_1{}^3\Sigma) \xrightarrow{k_D} \tag{1}$$

These complexes either dissociate back again with rate constant k_{-diff} or react forward spin-allowed: $^1(T_1{}^3\Sigma)$ to singlet ground-state sensitizer S_0 and $O_2(^1\Sigma_g{}^+)$ or $O_2(^1\Delta_g)$, $^3(T_1{}^3\Sigma)$ to S_0 and $O_2(^3\Sigma_g{}^-)$. The quintet complex $^5(T_1{}^3\Sigma)$ has no direct product channel. The overall rate constant k_D of product formation is calculated from $k_T{}^Q$ according to eq 2. The single rate constants $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$ are then obtained by eqs 3−5:[23−26]

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

$$k_T{}^{1\Sigma} = a k_D \quad (3)$$

$$k_T{}^{1\Delta} = (S_\Delta - a) k_D \quad (4)$$

$$k_T{}^{3\Sigma} = (1 - S_\Delta) k_D \quad (5)$$

The multiplicity-normalized rate constants $k_T{}^P/m$ (i.e., $k_T{}^{1\Sigma}/1$, $k_T{}^{1\Delta}/1$ and $k_T{}^{3\Sigma}/3$) depend for $T_1(\pi\pi^*)$ sensitizers with high oxidation potential and minimum CT interactions between T_1 and O_2 in a common way on the excess energy ΔE for formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ from $^{1,3}(T_1{}^3\Sigma)$ encounter complexes.[23−28] This finding led to the conclusion that the formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ proceeds from $^1(T_1{}^3\Sigma)$ and $^3(T_1{}^3\Sigma)$ encounter complexes with negligible CT character (= nCT complexes) being in a fully established intersystem crossing (ISC) equilibrium, see the left-hand side of Scheme 1.[23−28]

Internal conversion (IC) of the $^{1,3}(T_1{}^3\Sigma)$ nCT complexes occurs with rate constants $k_{\Delta E}{}^{1\Sigma}$, $k_{\Delta E}{}^{1\Delta}$, and $k_{\Delta E}{}^{3\Sigma}$ (= $k_{\Delta E}{}^P$) to lower-lying nCT complexes $^1(S_0{}^1\Sigma)$, $^1(S_0{}^1\Delta)$, and $^3(S_0{}^3\Sigma)$, which dissociate to the respective products. The IC is ruled by the energy gap relation $\log(k_{\Delta E}{}^P/m) = f(\Delta E)$ of eq 6 where ΔE is $E_T - E_\Sigma$, $E_T - E_\Delta$, or E_T, respectively.[23−26,28]

$$\log(k_{\Delta E}{}^P/m/\mathrm{s}^{-1}) = 9.05 + 9 \times 10^{-3}\Delta E - 1.15 \times 10^{-4}\Delta E^2 + 1.15 \times 10^{-7}\Delta E^3 + 9.1 \times 10^{-11}\Delta E^4 \quad (6)$$

The $k_T{}^P/m$ data of sensitizers with nonnegligible CT interactions deviate, however, significantly from this polynomial to larger values.[23−27] In this case, a second deactivation path is opened for $^{1,3}(T_1{}^3\Sigma)$ nCT complexes which leads via $^{1,3}(T_1{}^3\Sigma)$ exciplexes with CT character (= CT complexes) irreversibly also to the formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$, see the right-hand side of Scheme 1. Interestingly, no ISC equilibrium exists for $^{1,3}(T_1{}^3\Sigma)$ CT complexes in contrast to what has been found for the $^{1,3}(T_1{}^3\Sigma)$ nCT complexes. This different behavior has been explained by the stronger binding interactions between T_1 excited sensitizer and O_2 in the $^{1,3}(T_1{}^3\Sigma)$ exciplexes.[25] The rate constants for the formation of each O_2 product state are additively composed of the nCT component $k_{\Delta E}{}^P/m$ and the CT component $k_{CT}{}^P/m$.[23−26] Thus, values of $k_{CT}{}^P$ are obtained by eqs 7−9.

$$k_{CT}{}^{1\Sigma} = k_T{}^{1\Sigma} - k_{\Delta E}{}^{1\Sigma} \quad (7)$$

$$k_{CT}{}^{1\Delta} = k_T{}^{1\Delta} - k_{\Delta E}{}^{1\Delta} \quad (8)$$

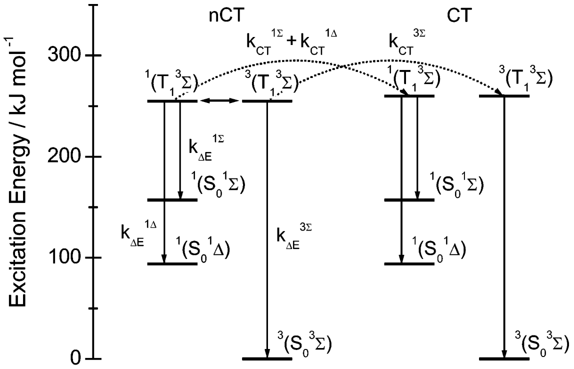
$$k_{CT}{}^{3\Sigma} = k_T{}^{3\Sigma} - k_{\Delta E}{}^{3\Sigma} \quad (9)$$

Investigations with three series of naphthalenes, biphenyls, and fluorenes in TET showed that the values of $\log(k_{CT}{}^P/m)$ for the formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ correlate for each homologues series of sensitizers at almost constant E_T nearly as parallels with the free energy difference $\Delta G_{CET} - C$ calculated according to the Rehm−Weller eq 10.[29,30]

$$\Delta G_{CET} = F(E_{OX} - E_{RED}) - E_T + C \quad (10)$$

ΔG_{CET}, F, and E_{RED} are the free energy change for complete electron transfer from the T_1-excited sensitizer to O_2, the Faraday constant, and the reduction potential of molecular oxygen (−0.78 V vs. SCE in acetonitrile)[31], respectively, and C is the electrostatic interaction energy. C depends strongly on solvent polarity but changes only little for the interactions of different aromatic sensitizers with the very small O_2 molecule in a given solvent.[30,32,33] Thus, CT-induced quenching of T_1-excited sensitizers by O_2 in a single solvent has mostly been discussed ignoring the value of C, i.e., with respect to the variation of $\Delta G_{CET} - C$ data.[8,10−14,23−26] The further analysis of the naphthalene, biphenyl, and fluorene data demonstrated that, on average, relations 11 and 12 hold true.[23−26]

SCHEME 1



$$k_{CT}{}^{3\Sigma} = 3 \times (k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta}) \quad (11)$$

$$k_{CT}{}^{1\Sigma} = 2 \times k_{CT}{}^{1\Delta} \quad (12)$$

Thus, rather simple quantitative relations determine the contributions of the nCT and CT pathways to the overall sensitization of singlet oxygen by $\pi\pi^*$ excited triplets. The relative contribution p_{CT} of CT-mediated deactivation calculated for a sensitizer of known triplet energy from its quenching rate constant is a quantitative measure of the balance between nCT and CT deactivation. Recently, we derived equations expressing the quenching rate constant $k_T{}^Q$ and the efficiencies a and S_Δ of $O_2(^1\Sigma_g{}^+)$ and overall $O_2(^1\Delta_g)$ sensitization as functions of p_{CT} vide infra. It was shown that these equations reproduce the variations of $k_T{}^Q$, a, and S_Δ caused by a shift of the balance from nCT to CT deactivation without even requiring any knowledge of sensitizer oxidation potentials E_{OX}.[34]

However, these findings were restricted to the solvent CCl_4, where the $O_2(^1\Sigma_g{}^+)$ lifetime is 130 ns, long enough for the quantitative determination of $O_2(^1\Sigma_g{}^+)$.[21,35,36] But due to the progress of detector technology, it is now possible to do such measurements also in solvents of much shorter $O_2(^1\Sigma_g{}^+)$ lifetimes. Very recently we studied the T_1 state quenching by O_2 in $CHCl_3$ and CD_3CN, solvents of very different polarity compared with CCl_4, and found that the empirical energy gap relation holds true, independent of solvent polarity.[28] Because the empirical energy gap relation also describes the excess energy dependence of rate constants of $O_2(^1\Delta_g)$ quenching by carotenoids,[37] it was concluded that it represents a generally valid energy gap law for the rate constants of electronic energy transfer to and from O_2 in the absence of CT interactions.[28]

CT interactions are sensitive to variations of the solvent polarity. In fact, Wilkinson and co-workers found in systematic studies on two series of differently substituted naphthalenes and biphenyls in cyclohexane (CHX), benzene (BNZ), and acetonitrile (ACN) that the increase of solvent polarity leads to a significant increase of $k_T{}^Q$ and a simultaneous decrease of S_Δ, which are more pronounced for sensitizers with strong CT interactions with O_2.[6,8,10,11,14] This very valuable data set will be used in the present study to investigate whether the recently derived quantitative relations describing singlet and ground-

TABLE 1: Oxidation Potentials E_{OX}, Triplet State Energies E_T, Differences $\Delta G_{CET} - C$, Rate Constants k_T^Q of Triplet Quenching by O_2, and Efficiencies S_Δ of Singlet Oxygen Sensitization for Biphenyls and Naphthalenes in Acetonitrile, Benzene, Cyclohexane, and Carbon Tetrachloride

	solvent			ACN		BNZ		CHX		TET	
compound	E_{OX} in ACN V vs. SCE	E_T kJ mol^{-1}	$\Delta G_{CET} - C$ kJ mol^{-1}	$k_T^Q/10^9$ M^{-1} s^{-1}	S_Δ	$k_T^Q/10^9$ M^{-1} s^{-1}	S_Δ	$k_T^Q/10^9$ M^{-1} s^{-1}	S_Δ	$k_T^Q/10^9$ M^{-1} s^{-1}	S_Δ
4,4-dimethoxybiphenyl	1.30 ^{a}	266^a	−65.3	12.6^a	0.31^a	9.15^b	0.31^b	–	–	11.4^c	0.347^c
4-methoxybiphenyl	1.53^a	270^a	−47.1	8.56^a	0.36^a	5.94^b	0.29^b	2.67^b	0.37^b	4.18^c	0.389^c
4,4-dimethylbiphenyl	1.69^a	269^a	−30.7	5.93^a	0.42^a	3.71^b	0.37^b	1.50^b	0.62^b	2.31^c	0.647^c
4-methylbiphenyl	1.80^a	272^a	−23.1	4.36^a	0.44^a	2.46^b	0.41^b	1.12^b	0.70^b	1.46^c	0.730^c
biphenyl	1.91^a	274^a	−14.5	2.85^a	0.48^a	1.51^b	0.51^b	0.78^b	0.75^b	0.981^c	0.721^c
4-chlorobiphenyl	1.96^a	269^a	−4.6	2.10^a	0.56^a	1.36^b	0.61^b	0.76^b	0.85^b	0.870^c	0.854^c
4-bromobiphenyl	1.95^a	266^a	−2.6	2.05^a	0.59^a	1.35^b	0.61^b	0.71^b	0.89^b	0.822^c	0.878^c
4,4-dichlorobiphenyl	2.02^a	265^a	5.2	1.77^a	0.58^a	1.00^b	0.89^b	0.90^b	0.83^b	0.782^c	0.900^c
4,4-dibromobiphenyl	2.01^a	265^a	4.2	1.46^a	0.67^a	1.07^b	0.71^b	0.66^b	0.92^b	0.782^c	0.950^c
4-cyanobiphenyl	2.11^a	265^a	13.8	0.88^a	0.84^a	0.82^b	0.79^b	0.43^b	0.96^b	0.642^c	0.942^c
1-methoxynaphthalene	1.26^d	256^d	−59.2	7.2^d	0.33^d	5.0^e	0.34^e	3.89^d	0.56^d	3.78^f	0.521^f
acenaphthene	1.34^d	250^d	−45.5	6.5^d	0.41^d	4.4^e	0.40^e	3.31^d	0.61^d	2.84^f	0.590^f
2-methoxynaphthalene	1.38^d	253^d	−44.6	5.3^d	0.44^d	3.5^e	0.50^e	2.74^d	0.74^d	2.34^f	0.750^f
1-methylnaphthalene	1.54^d	257^d	−33.2	3.2^d	0.60^d	2.6^e	0.56^e	2.06^d	0.84^d	1.70^f	0.808^f
1-ethylnaphthalene	1.54^d	250^d	−26.2	3.3^d	0.56^d	2.6^e	0.57^e	2.06^d	0.86^d	–	–
2-methylnaphthalene	1.61^d	253^d	−22.4	3.1^d	0.61^d	2.5^e	0.57^e	2.06^d	0.91^d	1.65^f	0.846^f
2-ethylnaphthalene	1.56^d	253^d	−27.2	3.3^d	0.62^d	2.5^e	0.59^e	2.06^d	0.88^d	–	–
naphthalene	1.65^d	255^d	−20.5	2.6^d	0.62^d	2.1^e	0.62^e	1.60^d	0.92^d	1.33^f	0.880^f
2-bromonaphthalene	1.90^d	255^d	3.6	1.7^d	0.77^d	1.5^e	0.66^e	1.37^d	1.0^d	–	–
1-fluoronaphthalene	1.72^d	251^d	−9.8	2.2^d	0.71^d	1.9^e	0.68^e	1.60^d	0.94^d	–	–
1-bromonaphthalene	1.77^d	247^d	−1.0	1.8^d	0.77^d	1.5^e	0.73^e	1.37^d	1.0^d	1.18^f	0.984^f
1-chloronaphthalene	1.75^d	248^d	−3.9	1.9^d	0.74^d	1.6^e	0.75^e	1.49^d	1.0^d	–	–
1-cyanonaphthalene	2.01^d	243^d	26.2	1.4^d	0.87^d	1.2^e	0.75^e	1.26^d	1.0^d	0.93^f	0.979^f
1-nitronaphthalene	–	231^e	–	1.5^e	0.89^e	1.3^e	0.83^e	1.50^e	0.91^e	–	–
2,6-dimethoxynaphthalene	1.14^d	253^d	−67.7	9.6^d	0.25^d	–	–	4.60^d	0.39^d	–	–
2,7-dimethoxynaphthalene	1.34^d	245^d	−40.5	6.6^d	0.44^d	–	–	3.14^d	0.72^d	–	–
2,6-dimethylnaphthalene	1.49^d	252^d	−33.0	4.1^d	0.56^d	–	–	2.44^d	0.86^d	2.03^f	0.795^f
2,3-dimethylnaphthalene	1.50^d	247^d	−27.0	3.9^d	0.58^d	–	–	2.31^d	0.83^d	–	–

^{a} Ref 10. ^{b} Ref 11. ^{c} Ref 24. ^{d} Ref 14. ^{e} Ref 8. ^{f} Ref 23.

state oxygen formation as a function of p_{CT} are independent of solvent polarity and, thus, of general validity. To complete the solvent-dependent data, we include also the k_T^Q and S_Δ data obtained for two series of naphthalenes and biphenyls in CCl_4 (TET) in that analysis.[23,24]

Data

Table 1 collects quantitative literature data on the triplet sensitization of singlet oxygen by two series of biphenyl and naphthalene derivatives in four solvents published mainly by the group of Wilkinson. The values of k_T^Q critically depend on the oxygen concentrations assumed for different liquids. Wilkinson and co-workers used for air saturated solvents at room-temperature values of $[O_2]$ of 1.9×10^{-3} M for ACN and BNZ and 2.4×10^{-3} M for CHX, which are given by Murov et al. for these solvents at O_2 partial pressures of 0.21 bar.[10,11,38] The value for CHX was later corrected by Wilkinson to 2.1×10^{-3} M and the previous values of k_T^Q of the naphthalenes have correspondingly been corrected by multiplying with the ratio 2.4/2.1.[14] These data are listed in Table 1. The assumption that the O_2 concentration of air saturated solvents corresponds to the $[O_2]$ data given by Murov et al. for 0.21 bar O_2 partial pressure holds only for solvents with negligible vapor pressure. Actually, $[O_2] = 0.21(P_A - P_V)[O_2]_{P=1}$ should be used for air-saturated solvents, where P_A and P_V are the atmospheric and the solvent vapor pressure and $[O_2]_{P=1}$ is the O_2 concentration of the solvent at 1.013 bar O_2 partial pressure. With $[O_2]_{P=1} = 11.5 \times 10^{-3}$ M given by Murov et al. for CHX at 25 °C and with $P_V = 0.121$ bar, we obtain $[O_2] = 2.12 \times 10^{-3}$ M in agreement with Wilkinson's corrected value. Because the original k_T^Q data of the biphenyls in CHX listed in Table 1 have been calculated with $[O_2] = 2.4 \times 10^{-3}$ M, we correct them for the further analysis by multiplication with the ratio 2.4/2.12. $[O_2] = 1.71 \times 10^{-3}$ M is obtained for air saturated BNZ at 25 °C from Murov's value and $P_V = 0.101$ bar. Therefore, the corresponding k_T^Q data of the biphenyls and naphthalenes of Table 1 are multiplied by 1.9/1.71 before analysis. The value $[O_2] = 1.9 \times 10^{-3}$ M for ACN at 0.21 bar O_2 could not be traced to an original paper. Reference 39 given by Murov et al. describes not the origin of the $[O_2]$ value. Therefore, we take $[O_2] = 0.00242$ M determined recently for air-saturated CH_3CN at 25 °C by photooxygenation techniques to be more realistic and multiply all k_T^Q data of Table 1 corresponding to ACN by1.9/2.42.[40] The k_T^Q values of Table 1 for TET have been calculated with $[O_2] = 0.00228$ M resulting for air saturated conditions at 23 °C from $P_V = 0.121$ bar and $[O_2]_{P=1} = 12.4 \times 10^{-3}$ M.[38] The small corrections described lead to a weaker solvent polarity dependence of the k_T^Q data. It is obvious that these graduations rely on the accuracy of the solubility data which may differ from solvent to solvent. The following values have been taken for the diffusion-controlled rate constant k_{diff} for bimolecular processes with O_2: 4.50×10^{10} M^{-1} s^{-1} in ACN,[11] 3.33×10^{10} M^{-1} s^{-1} in BNZ,[11] 2.72×10^{10} M^{-1} s^{-1} in CHX,[11] and 2.72×10^{10} M^{-1} s^{-1} in TET.[23] We calculate the rate constant of back dissociation k_{-diff} in all solvents by $k_{-diff}/k_{diff} = 1$ M, where M is the unit mole per liter, as was already done by Gijzeman et al.,[4] byWilkinson et al.,[10,11] and by us in our previous works.[23−28,32−34,37]

Values of S_Δ and k_T^Q can sporadically be found for some compounds in some solvents at different places in the literature. These scattered data are, however, not suited for an accurate investigation of the influence of the solvent polarity on the triplet state quenching by O_2, due to their unknown accuracy. The solvent-dependent data used in the present analysis have been determined using the same advanced method, i.e., populating the singlet oxygen sensitizer triplet states indirectly by triplet−triplet energy transfer from primarily excited ketones with complete intersystem crossing.

Discussion

Relative Contribution of CT Deactivation. In the following, relations are presented that illustrate the variation of S_Δ and k_T^Q with a shift of the balance between the nCT and CT deactivation. This balance is easily described by the quantity p_{CT}, defined as relative contribution of CT deactivation referred to the overall deactivation of T_1 by O_2.[34] If the sensitizer triplet energy is known, the absolute contribution of the nCT path to deactivation, $\Sigma k_{\Delta E}^P = k_{\Delta E}^{1\Sigma} + k_{\Delta E}^{1\Delta} + k_{\Delta E}^{3\Sigma}$, is calculated by the energy gap law of eq 6 via the corresponding excess energies ΔE. The absolute contribution of the CT path is then simply $\Sigma k_{CT}^P = k_D - \Sigma k_{\Delta E}^P$. Thus, p_{CT} is obtained as an empirical parameter by eq 13, if E_T and k_T^Q are known.

$$p_{CT} = (k_D - \Sigma k_{\Delta E}^P)/k_D \qquad (13)$$

Equations 11 and 12 imply $k_{CT}^{1\Sigma} = \Sigma k_{CT}^P/6$, $k_{CT}^{1\Delta} = \Sigma k_{CT}^P/12$, and $k_{CT}^{3\Sigma} = 3 \times \Sigma k_{CT}^P/4$. Because $k_D = \Sigma k_{\Delta E}^P/(1 - p_{CT})$ and $\Sigma k_{CT}^P = p_{CT}\Sigma k_{\Delta E}^P/(1 - p_{CT})$ hold true, we derive eqs 14 and 15, which express the quantities S_Δ and k_T^Q in dependence of p_{CT}.[34]

$$S_\Delta = \{(k_{\Delta E}^{1\Sigma} + k_{\Delta E}^{1\Delta})(1 - p_{CT}) + p_{CT}\Sigma k_{\Delta E}^P/4\}/\Sigma k_{\Delta E}^P \qquad (14)$$

$$k_T^Q = \{k_{diff}\Sigma k_{\Delta E}^P/(1 - p_{CT})\}/\{k_{-diff} + \Sigma k_{\Delta E}^P/(1 - p_{CT})\} \qquad (15)$$

Equations 6 and 13−15 and the experimental values of E_T, S_Δ, and k_T^Q of Table 1 are used in the present study to evaluate values of p_{CT} for the sensitizers of the naphthalene and biphenyl series in the different solvents. The optimum value of p_{CT} is obtained for each sensitizer by variation of p_{CT} until the sum of the squared differences of calculated and experimental S_Δ and k_T^Q data reaches the minimum. Figures 1 and 2 illustrate the goodness of the resulting p_{CT} values by a comparison of S_Δ and $\log(k_T^Q)$ data calculated by eqs 14 and 15 with the respective experimental values.

The scatter of the S_Δ data around the straight line, which represents the identity of calculated and experimental values, is rather small for the biphenyls of Figure 1. For the naphthalenes, however, larger deviations of calculated values of S_Δ to smaller numbers have to be noted for the solvent CHX. Interestingly, most of the S_Δ data of the naphthalenes in CHX of Table 1 have been taken by Wilkinson et al. from an earlier original publication,[8] in which the authors already noted systematic deviations of the experimental S_Δ data to too large values. This became most obvious by the maximum value of $S_\Delta = 1.04$ measured for 1-bromonaphthalene. The authors suspected that a too large assumed value of $S_\Delta = 0.92$ for the reference sensitizer naphthalene could be the source of the deviations. But almost all of these previously determined S_Δ data including $S_\Delta = 0.92$ for naphthalene have been taken to their following work,[14] and in doing so, values exceeding unity have been set to 1.0, see Table 1.

Thus, the S_Δ data for the naphthalenes in CHX could well be systematically too large. Because the sensitization of singlet oxygen by naphthalenes has also been investigated in a second nonpolar solvent (TET), we neglect in the further analysis naphthalene data in CHX. In doing so, we state a satisfying agreement of calculated and experimental S_Δ and $\log(k_T^Q)$ data in polar and nonpolar solvents supporting the applied model, see Figures 1 and 2. It should be noted that the range of variation of $\log(k_T^Q)$ is smaller for the naphthalenes than for the biphenyls, despite their even larger variation of $\Delta G_{CET} - C$, see Table 1.

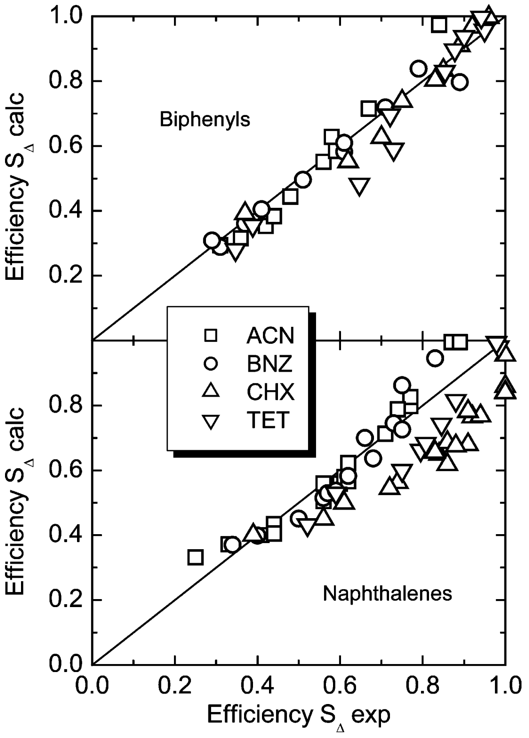


Figure 1. Efficiency S_Δ of overall $O_2(^1\Delta_g)$ formation during T_1 state quenching by O_2 for biphenyls and naphthalenes in different solvents. Deviations of calculated values from experimental data.

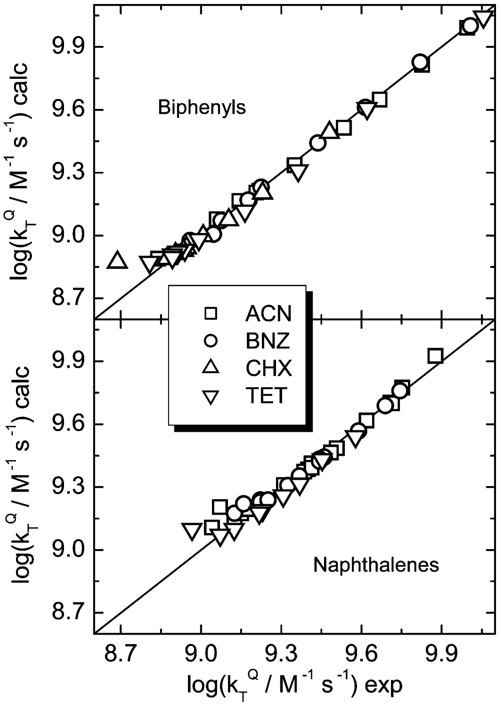


Figure 2. Rate constant k_T^Q of T_1 state quenching by O_2 for biphenyls and naphthalenes in different solvents. Deviations of calculated values of $\log(k_T^Q)$ from experimental $\log(k_T^Q)$ data.

The optimum p_{CT} values evaluated in this way are used to illustrate in the lower part of Figure 3 the variation of S_Δ for the change from pure nCT to predominant CT deactivation. Equation 14 predicts for CT deactivation $S_\Delta = 0.25$ because of

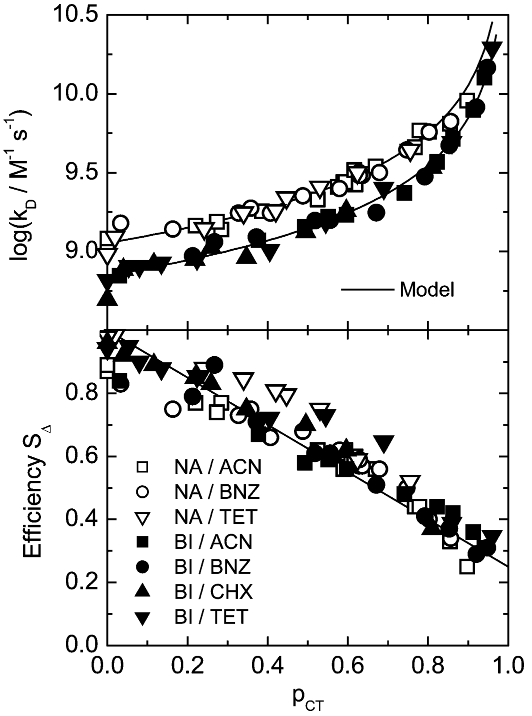


Figure 3. Variation of the logarithms of the overall rate constant of $^{1,3}(T_1{}^3\Sigma)$ complex deactivation, $\log(k_D)$, (upper part) and of the efficiencies of overall formation of $O_2(^1\Delta_g)$, S_Δ, (lower part) with p_{CT} for biphenyls and naphthalenes in different solvents.

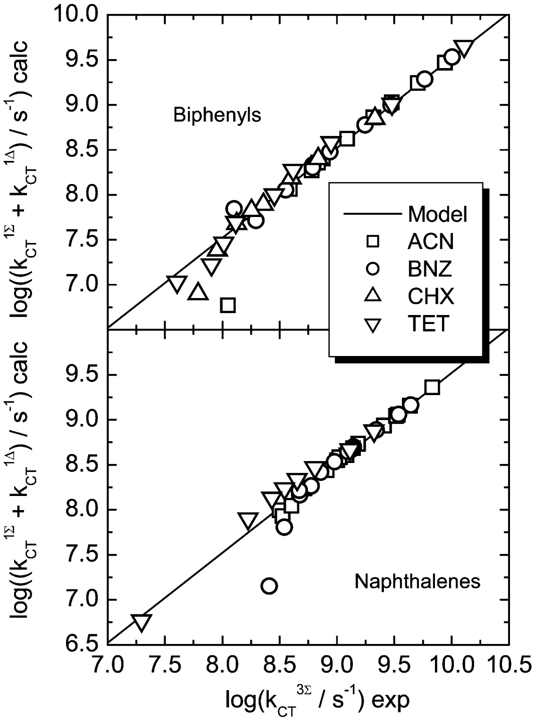


Figure 4. Correlations of $\log(k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta})$ calculated from values of $\Sigma k_{\Delta E}{}^{P}$ and p_{CT} versus experimental data of $\log(k_{CT}{}^{3\Sigma})$ for biphenyls and naphthalenes in different solvents.

$p_{CT} = 1$. S_Δ depends via eqs 6 and 14 on the value of E_T in the case of pure nCT deactivation. S_Δ approaches unity if $E_T \gg E_\Sigma$, because then, according to eq 6, $k_{\Delta E}{}^{3\Sigma}$ becomes very small. This holds true for the biphenyls and naphthalenes with average values of $S_\Delta > 0.995$ calculated for $p_{CT} = 0$. The straight line in the lower part of Figure 3 represents the expected linear decrease of S_Δ with an increasing value of p_{CT} and describes the experimental variation rather well. No significant systematic deviations are observed.

The upper part of Figure 3 displays the dependence of $\log(k_D)$ on p_{CT}. The calculation of a common dependence of $\log(k_T{}^Q)$ on p_{CT} is not possible for a single series of sensitizers in different solvents. The weakening of the variation of $\log(k_T{}^Q)$ with p_{CT}, which occurs when $k_T{}^Q$ approaches the value of k_{diff}, would vary with solvent due to the differences of k_{diff}. These problems are absent in the analysis of $\log(k_D)$ data. A general nonlinear increase of $\log(k_D)$ with p_{CT} is observed for both sensitizer series. However, the naphthalenes are distinguished by larger $\log(k_D)$ values throughout the whole p_{CT} range. The solid lines represent the dependences calculated by $k_D = \Sigma k_{\Delta E}{}^P/(1 - p_{CT})$, eq 13 rearranged, using average values of $\Sigma k_{\Delta E}{}^P$ for each sensitizer series. The curves describe both dependences very well. The larger values of $\log(k_D)$ of the naphthalenes are the consequence of their smaller triplet energies compared with the biphenyls leading via eq 6 to larger sums $\Sigma k_{\Delta E}{}^P$ and to the smaller variation of $\log(k_D)$. The difference in E_T is therefore also the reason for the smaller range of $\log(k_T{}^Q)$ data of the naphthalenes compared with the biphenyls, see Figure 2. Both plots of Figure 3 demonstrate that the two-channel deactivation model, illustrated in Scheme 1 and quantified by eqs 1−9 and 11−13, reproduces the experimental data of the naphthalenes and biphenyls in solvents of very different polarity as well. Thus, a consistent and reasonable mechanism for $T_1(\pi\pi^*)$ state quenching by O_2 has been evolved surpassing previous advanced models.[10,11,14] It is most interesting that the empirical parameter p_{CT} determines the balance between nCT and CT deactivation for every sensitizer without the knowledge of oxidation potential and solvent polarity.

The Effect of Solvent Polarity on CT Deactivation. The values of $\log(k_{CT}{}^{1\Sigma})$, $\log(k_{CT}{}^{1\Delta})$, and $\log(k_{CT}{}^{3\Sigma})$, correlate for homologues series of sensitizers with almost constant E_T nearly as parallels with $\Delta G_{CET} - C$.[23−25] Furthermore, CT deactivation forms $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ in the product ratio (1/6):(1/12):(3/4). If this is valid also for the data set under investigation, linear correlations between $\log(k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta})$ and $\log(k_{CT}{}^{3\Sigma})$ with slope unity and intercept log(1/3) are expected in any solvent. For verification, we calculate experimental rate constants $k_T{}^{3\Sigma}$ by eq 5. $k_{CT}{}^{3\Sigma} = k_T{}^{3\Sigma}$ holds true in good approximation, because the average values of $k_{\Delta E}{}^{3\Sigma}$ for the naphthalenes (5.2×10^6 s^{-1}) and for the biphenyls (2.3×10^6 s^{-1}) are at least 1 order of magnitude smaller than the values of $k_T{}^{3\Sigma}$. The sum $k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta}$ is obtained for every sensitizer from $\Sigma k_{\Delta E}{}^P$ and p_{CT} by $k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta} = p_{CT}\Sigma k_{\Delta E}{}^P/(4 \times (1 - p_{CT}))$. Figure 4 plots the correlations $\log(k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta})$ versus $\log(k_{CT}{}^{3\Sigma})$ for the biphenyls and naphthalenes.

The data match the expected correlation indicated by the straight lines very well as long as $\log(k_{CT}{}^{3\Sigma}) > 8.5$. The scatter of the data increases drastically below that threshold because of the strongly increasing uncertainty of the experimental values of $\log(k_{CT}{}^{3\Sigma})$. Figure 4 demonstrates that CT interactions affect the formation of singlet oxygen and ground-state oxygen with the same strength. Thus, also in the more polar solvents, $^1(T_1{}^3\Sigma)$ and $^3(T_1{}^3\Sigma)$ exciplexes are formed in a parallel way from the fully established ISC equilibrium of $^{1,3}(T_1{}^3\Sigma)$ encounter complexes in agreement with the relation $\Sigma k_{CT}{}^P = 4 \times k_{CT}{}^{3\Sigma}/3$.

Values of $\log(k_{CT}{}^{3\Sigma})$ of homologues series of sensitizers with almost constant E_T decrease approximately linearly with increasing $\Delta G_{CET} - C$.[8,10,11,14,23−25] The slopes of these correlations are by factors β smaller than the limiting slope $-0.434/(RT)$ for electron-transfer reactions in the endergonic range. β has been determined as 0.188 and 0.160 for the biphenyls and naphthalenes, respectively, in TET,[23,24] and decreases with

TABLE 2: Coulomb Interaction Energies *C* of Sensitizer$^+$/O$_2$$^-$ Radical Ion Pairs, Reorganization Energies *λ*, Corrective Factors *f*, and Charge Transfer Characters *δ* of $^{1,3}(T_1{}^3\Sigma)$ Exciplexes

system	C^a kJ mol^{-1}	λ kJ mol^{-1}	λ^b kJ mol^{-1}	f	f^b	δ	δ^b
biphenyls/ACN	−7.3	86.3	86.0	0.276	0.333	0.53	0.58
biphenyls/BNZ	67.5^c	49.1	–	0.229	–	0.48	–
biphenyls/TET	133.6	20.1	27.4	0.184	0.183	0.43	0.43
naphthalenes/ACN	−7.6	88.9	91.7	0.231	0.346	0.48	0.59
naphthalenes/BNZ	67.4^c	60.7	–	0.139	–	0.37	–
naphthalenes/TET	134.0	37.3	33.6	0.187	0.195	0.43	0.44

[a] Calculated by eq 16. [b] From ref 33. [c] Using an effective value $\epsilon = 4$ for BNZ.

increasing solvent polarity from 0.170 (CHX) to 0.145 (BNZ) and 0.125 (ACN) for the biphenyls and from 0.170 (CHX) to 0.125 (ACN) for the naphthalenes.[10,11,14] The factor β has been interpreted in a very simplified picture as the fraction of charge transfer of the $^3(T_1{}^3\Sigma)$ exciplex,[8,10,11,14,23−25] or of the transition state passed on the way to the $^3(T_1{}^3\Sigma)$ exciplex.[11−14] However, the inverse dependence of the CT character on solvent polarity is very surprising, as it contradicts the observed increase of CT character of pure aromatic exciplexes with increasing solvent polarity.[41]

Therefore, linear free energy relationships (LFERs) seem to be no appropriate tool in the analysis of the CT-induced T_1 state quenching by O_2 in solvents of different polarity. Furthermore, the nonconsideration of the electrostatic interaction energy C required for the evaluation of ΔG_{CET} by eq 10 is of course a rough simplification suited for data collected in one single solvent. However, the consideration of C is indispensable if rate constants from solvents of different polarity are compared. If the values of E_{OX} and E_{RED} used in eq 10 have been determined in acetonitrile, C can be calculated by eq 16 derived by Weller,[30]

$$C = \frac{e^2}{2}\left(\frac{1}{r^+} = \frac{1}{r^-}\right)\left(\frac{1}{\epsilon} - \frac{1}{37}\right) - \frac{e^2}{\epsilon(r^+ + r^-)} \qquad (16)$$

where e is the elementary charge ($e^2 = 14.43$ eV Å) and ϵ is the relative permittivity of the solvent. The radii of the donor molecules vary only little in both series of sensitizers. Assuming a spherical molecular shape, average values of r^+ of 3.44 Å (biphenyls) and 3.23 Å (naphthalenes) and of $r^- = 1.73$ Å (O_2) result from the corresponding van der Waals volumes.[32,33] Using these numbers and $\epsilon = 2.238$ (TET) and $\epsilon = 37$ (ACN), we calculate the Coulomb term C as given in Table 2. The estimation of C is less straightforward for BNZ because the solvation free energy of polar solutes by BNZ is not appropriately described via its relative permittivity $\epsilon = 2.284$. According to Dimroth's empirical solvent polarity scale, benzene ($E_T(30) = 34.5$) has a similar effective polarity like diethyl ether ($E_T(30) = 34.6$, $\epsilon = 4.335$).[42] Thus, we estimate the Coulomb interaction energies of Table 2 for BNZ with an effective ϵ of 4. Inserting these numbers into eq 10 yields more realistic values of the change of free energy ΔG_{CET} for a complete electron transfer from T_1 excited sensitizer to O_2. However, it should be noted that in the present case of CT-induced deactivation, no electron transfer but only charge transfer takes place.

Recently, we found that for biphenyls and naphthalenes, the rate constants of CT-induced quenching of T_1 excited sensitizers by O_2 and of CT-induced quenching of $O_2(^1\Delta_g)$ by ground-state sensitizers of the same series follow a common dependence on ΔG_{CET}, if the different spin-statistical weights of the initial steps of quenching (1/3 for T_1, 1 for $O_2(^1\Delta_g)$) are taken into account. This was done by multiplying $k_{CT}{}^{3\Sigma}$ by the factor 3.[32,33] Using these larger data sets that cover a much broader range of ΔG_{CET} than the present data we realized that the use of a parabolic Marcus-type relationship leads to a consistent and much better description of CT-induced deactivation than the use of LFERs. Experimental activation free energies $\Delta G^{\#}$ of CT complex formation have been obtained from eq 17,

$$\Delta G^{\#} = -RT \ln\left(\frac{k_{CT}}{k_B T/h}\right) \qquad (17)$$

where k_B and h are the Boltzmann and Planck constants, T is the Kelvin temperature, and k_{CT} stands for both $3 \times k_{CT}{}^{3\Sigma}$ and the rate constant of CT-induced quenching of $O_2(^1\Delta_g)$, respectively. We described $\Delta G^{\#}$ by eq 18, which differs from the classical Marcus equation by the factor f. f accounts for the fact that the actual free energy change of exciplex formation ΔG_{CT} is unknown but expected to be proportional to the free energy change ΔG_{CET} for a complete electron transfer to oxygen. Fits of the data to eq 18

$$\Delta G^{\#} = \frac{\lambda}{4}\left(1 + \frac{f\Delta G_{CET}}{\lambda}\right)^2 \qquad (18)$$

were rather smooth and yielded two parameters related to the CT character δ of the exciplexes: the reorganization energy λ, describing the energetic requirements for the reorganization of the complex and its surroundings in the charge-transfer step, and the corrective factor f defined by eq 19.[32,33]

$$f = \Delta G_{CT}/\Delta G_{CET} \qquad (19)$$

We use this Marcus-type parabolic model now for the analysis of the rate constants of the CT-induced quenching of T_1 states by O_2 of the present data set. Calculating $\Delta G^{\#}$ via $k_{CT} = 3 \times k_{CT}{}^{3\Sigma}$ and eq 17 and fitting $\Delta G^{\#}$ as a function of ΔG_{CET} to eq 18, we obtain for each data set values of λ and f as fit parameters. These are listed in Table 2. Values of the free-energy change of exciplex formation ΔG_{CT} are then obtained by eq 19. Figure 5 illustrates the dependences of the experimental data of $\Delta G^{\#}$ on ΔG_{CT}.

The resulting fit curves, which are drawn as solid lines, describe the experimental data quite well. Although the range of ΔG_{CET} is distinctly smaller than in the previous combined analysis of T_1 *and* $O_2(^1\Delta_g)$ deactivation, still similar values of λ and f are obtained, see Table 2 for comparison. An increase of the reorganization energy with solvent polarity is observed for both series of sensitizers, which is expected for the formation of exciplexes.[41,43] In our recent detailed analysis of the CT-induced T_1 and $O_2(^1\Delta_g)$ deactivation, we found that the CT character δ of the exciplexes formed can be estimated by the empirical relation $\delta \approx f^{1/2}$.[32,33] Using this equation, we obtain for the biphenyls a significant increase of the CT character of the $^3(T_1{}^3\Sigma)$ exciplexes with solvent polarity from 0.43 (TET) over 0.48 (BNZ) to 0.53 (ACN), which is in line with the experimentally observed increase of the CT character of pure aromatic exciplexes with increasing solvent polarity.[41] Thus,

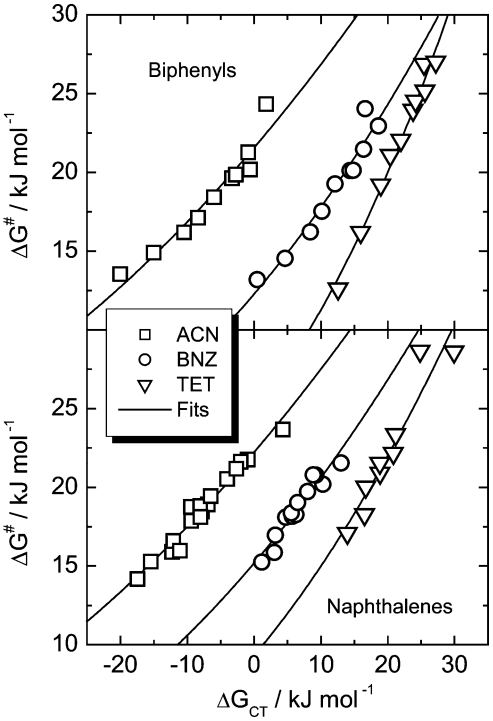


Figure 5. Dependences of the activation free energy $\Delta G^{\#}$ of $^3(T_1{}^3\Sigma)$ exciplex formation on the corresponding free energy ΔG_{CT} for biphenyls and naphthalenes in different solvents.

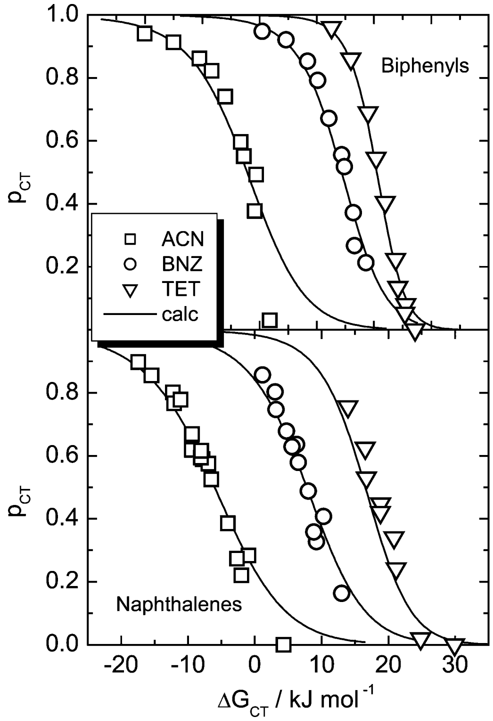


Figure 6. Change of the balance between nCT and CT deactivation, described by p_{CT}, upon variation of the free energy ΔG_{CT} of $^{1,3}(T_1{}^3\Sigma)$ exciplex formation for biphenyls and naphthalenes in different solvents.

the contradictions resulting from the interpretation of the factor β of LFERs as fraction of CT of the $^3(T_1{}^3\Sigma)$ exciplex or of the corresponding transition state, which led to the strange decrease of the CT character with increasing solvent polarity, are removed if the Marcus-type parabolic analysis is applied.

The slopes *sl* of the fits of Figure 5 are given by $sl = 0.5 + (0.5/\lambda) \times \Delta G_{CT}$. This relation explains why the slopes decrease with increasing reorganization energy λ and, thus, with increasing solvent polarity. Therefore, larger slopes result for TET (or CHX) for both the parabolic representations of $\Delta G^{\#}$ vs. ΔG_{CT} and for the LFER representations of $\log(k_{CT}{}^{3\Sigma})$ vs. $\Delta G_{CET} - C$, which caused the wrong impression of stronger CT effects in nonpolar solvents. The picture is less stringent for the naphthalenes due to the smaller range of $\Delta G^{\#}$ and ΔG_{CT} data leading to a larger uncertainty of the fit parameters. Actually, *f* deviates to lower values for BNZ being distinguished by the smallest $\Delta G^{\#}$ and ΔG_{CT} range, see Figure 5. But *f* and δ increase with solvent polarity if one compares TET with ACN.

Figure 5 gives also information about the change of the free energy of formation of $^{1,3}(T_1{}^3\Sigma)$ exciplexes from $^{1,3}(T_1{}^3\Sigma)$ encounter complexes. Exciplex formation is mainly exergonic ($-20 \leq \Delta G_{CT} \leq 2$ kJ mol^{-1}) in ACN and endergonic ($13 \leq \Delta G_{CT} \leq 27$ kJ mol^{-1}) in TET for the biphenyls. Similar ranges hold true for the naphthalenes. Thus, the exciplexes of triplet excited sensitizer and O_2 are moderately stabilized by 25−30 kJ mol^{-1} in going from nonpolar to highly polar solvents.

The Effect of Solvent Polarity on the Balance Between nCT and CT Deactivation. The empirical parameter p_{CT} defined by eq 13 evaluates the balance between nCT and CT deactivation surprisingly without knowledge of the sensitizer oxidation potential and the solvent polarity. But p_{CT} depends via $\Sigma k_{\Delta E}{}^{P}$ on the triplet state energy and via $\Sigma k_{CT}{}^{P}$ on the strength of CT interactions, which vary with E_T, oxidation potential, and solvent polarity, see eq 20.

$$p_{CT} = \Sigma k_{CT}{}^{P} / (\Sigma k_{CT}{}^{P} + \Sigma k_{\Delta E}{}^{P}) \qquad (20)$$

The very good correlations of $\log(k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta})$ with $\log(k_{CT}{}^{3\Sigma})$ with slope unity and intercept log(1/3) shown in Figure 4 imply that the reorganization energies λ, the correction factors *f*, and the corresponding solvent polarity dependences hold true for the formation of singlet and triplet $(T_1{}^3\Sigma)$ exciplexes and for the sum $\Sigma k_{CT}{}^{P}$ as well. Thus, we evaluate on the basis of the fit parameters given in Table 2 (i) ΔG_{CT} from ΔG_{CET} and *f* by eq 19, (ii) $\Delta G^{\#}$ from ΔG_{CET}, λ, and *f* by eq 18, (iii) $k_{CT}{}^{3\Sigma} = k_{CT}/3$ from $\Delta G^{\#}$ by eq 17, and (**iv**) $\Sigma k_{CT}{}^{P} = 4 \times k_{CT}{}^{3\Sigma}/3$. Using the respective average values of $\Sigma k_{\Delta E}{}^{P}$ for the biphenyls and for the naphthalenes, we finally calculate via eq 20 functions $p_{CT} = f(\Delta G_{CT})$. Figure 6 compares the experimentally derived optimum p_{CT} data with $p_{CT} = f(\Delta G_{CT})$ for both sensitizer series in ACN, BNZ, and TET. The calculated sigmoidals $p_{CT} = f(\Delta G_{CT})$ describe the experimental p_{CT} values with one exception very good. Only the curve calculated for the naphthalenes in TET is shifted from the p_{CT} data but barely by about 1 kJ mol^{-1} to lower ΔG_{CT}. This moderate deviation would already vanish with a 15% smaller value of $\Sigma k_{\Delta E}{}^{P}$. Thus, the quantitative relations which determine singlet and ground-state oxygen formation as a function of p_{CT} are valid for solvents of very different polarity.

The shift from nCT to CT deactivation occurs for each of the systems in a rather narrow ΔG_{CT} range. The ranges get broader with increasing solvent polarity mainly due to the increase of *f* spreading the ΔG_{CT} range. All sigmoidals of the naphthalenes are placed to lower ΔG_{CT} values compared with the biphenyls. The reason for that displacement are the larger $\Sigma k_{\Delta E}{}^{P}$ values of the naphthalenes. Therefore, correspondingly larger sums $\Sigma k_{CT}{}^{P}$ are necessary to reach $p_{CT} = 0.5$, which requires stronger CT interactions and more negative ΔG_{CT} values for the naphthalenes. Thus, triplet state energy and oxidation potential of the sensitizer and the solvent polarity are the actual parameters determining the balance between nCT and CT deactivation described by p_{CT}.

Conclusions

A mature model has been evolved that quantitatively reproduces kinetic data on the sensitization of singlet oxygen for T_1-($\pi\pi^*$) sensitizers of various triplet energies in solvents of strongly different polarities.[23−28,34] This model is illustrated by Scheme 1 and differs from earlier-developed kinetic schemes of the Wilkinson group mainly by the fully established ISC equilibrium of the $^{1,3}(T_1{}^3\Sigma)$ nCT complexes from which IC to lower-lying nCT complexes $^1(S_0{}^1\Sigma)$, $^1(S_0{}^1\Delta)$, and $^3(S_0{}^3\Sigma)$ occurs controlled by the energy gap law of eq 6. The schemes of Wilkinson and co-workers exclude ISC between $^1(T_1{}^3\Sigma)$ and $^3(T_1{}^3\Sigma)$ nCT complexes and allow only formation of $O_2(^1\Sigma_g{}^+)$ and $O_2(^1\Delta_g)$ but not formation of $O_2(^3\Sigma_g{}^-)$ in the nCT deactivation channel.[10,11,14,20] However, this assumption is in conflict with the energy gap law of eq 6, which just recently has been shown to hold true not only in TET but in other solvents as well.[28]

Scheme 1 rests on the competition of a nCT and a CT deactivation channel for the T_1 state quenching by O_2 both leading to formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$. If CT interactions are important, $^1(T_1{}^3\Sigma)$ and $^3(T_1{}^3\Sigma)$ exciplexes are formed from $^{1,3}(T_1{}^3\Sigma)$ encounter complexes in competition to IC. It is found that only this reaction is influenced by the solvent polarity. The rate constants of exciplex formation depend on the corresponding free energy change ΔG_{CT} calculated by a Marcus-type parabolic model. ΔG_{CT} varies with sensitizer triplet energy, oxidation potential, and solvent polarity. The $^{1,3}(T_1{}^3\Sigma)$ exciplexes are moderately stabilized by 25−30 kJ mol^{-1} in going from nonpolar to highly polar solvents. In contrast to previous applied models, the parabolic model yields the expected increase of the CT character of exciplexes with solvent polarity. The balance between both deactivation channels is described by the relative contribution p_{CT} of CT mediated deactivation. p_{CT} varies for sensitizer series with almost constant triplet energy as sigmoidal with ΔG_{CT}. The change of p_{CT} strongly influences the rate constant of overall quenching of the triplet state by O_2 and the efficiency of singlet oxygen formation. The quantitative model illustrated by Scheme 1 represents a realistic and general mechanism for the quenching of $\pi\pi^*$ triplet states by O_2 surpassing previous advanced models.

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