228 *J. Phys. Chem. A* **2002,** *106,* 228−235

Formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ during Oxygen Quenching of $n\pi^*$ Triplet Phenyl Ketones: The Role of Charge Transfer and Sensitizer-Oxygen Complex Structure

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Received: August 30, 2001

Rate constants of formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ in the quenching of triplet states T_1 by O_2 have been determined for a series of nine benzophenones (BPs) of strongly varying oxidation potential, E_{ox}, but almost constant triplet-state energy E_T. These data are analyzed considering data determined previously for $T_1(\pi\pi^*)$ sensitizers of very different E_T and E_{ox}. Much weaker charge transfer (CT) effects are observed for the $T_1(n\pi^*)$ BPs compared with those obtained with a series of structurally related $T_1(\pi\pi^*)$ biphenyls. The quenching proceeds for $T_1(n\pi^*)$ and $T_1(\pi\pi^*)$ sensitizers 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 channel originates from excited $^{1,3}(T_1{\cdot}^3\Sigma)$ complexes with no CT character and the other from $^{1,3}(T_1{\cdot}^3\Sigma)$ exciplexes with partial CT character. Different energy gap relations determine the formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ of $T_1(\pi\pi^*)$ and $T_1(n\pi^*)$ sensitizers in the nCT channel, whereby the excess energy (ΔE) dependence of the corresponding rate constants is much weaker for the $T_1(n\pi^*)$ ketones. In the pCT channel, the respective rate constants vary on a logarithmic scale linearly with the free energy change for complete electron transfer for both $T_1(\pi\pi^*)$ and $T_1(n\pi^*)$ sensitizers. This dependence too is much weaker for $T_1(n\pi^*)$ than for $T_1(\pi\pi^*)$ sensitizers. The comparison with CT induced quenching of $O_2(^1\Delta_g)$ by ground-state sensitizers reveals that the different electronic configurations leads to different sterical structures of $^{1,3}(T_1(n\pi^*){\cdot}^3\Sigma)$ and $^{1,3}(T_1(\pi\pi^*){\cdot}^3\Sigma)$ complexes. These differences strongly influence the complex deactivation and explain both the weaker ΔE dependence and the weaker CT effects in the quenching of $T_1(n\pi^*)$ by O_2.

Introduction

The quenching of excited triplet states T_1 of many compounds by molecular oxygen O_2 produces singlet oxygen. Both lowest electronically excited singlet states $^1\Sigma_g^+$ (= $^1\Sigma$) and $^1\Delta_g$ (= $^1\Delta$) and the $^3\Sigma_g^-$ (= $^3\Sigma$) ground state of O_2 are formed in competition, 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] However, $O_2(^1\Sigma_g^+)$ is very rapidly and completely deactivated by electronic-to-vibrational energy transfer to the metastable and highly reactive $O_2(^1\Delta_g)$ of excitation energy $E_\Delta = 94$ kJ mol^{-1},[5,8] which is the commonly called singlet oxygen and which is involved as intermediate in many important photoprocesses, such as photodynamic inactivation of viruses and cells, phototherapy of cancer, photocarcinogenesis, and photodegradation of dyes and polymers.

Rate constants k_T^Q of T_1 state quenching and quantum yields of singlet oxygen sensitization have been measured for hundreds of sensitizers because of its importance.[9−21] It was found that k_T^Q first decreases with increasing E_T.[11] But this energy dependence is reverted in the high E_T region, due to increasing charge-transfer interactions,[12,13] which also imply a decrease in the efficiencies S_Δ of overall $O_2(^1\Delta_g)$ sensitization in the quenching of the T_1 state by O_2 with increasing E_T and with decreasing oxidation potential E_{ox} of the sensitizer.[14−21] Charge transfer and noncharge transfer effects could, however, quantitatively be separated only when the determination of the efficiencies a and b (= $S_\Delta - a$) of the direct formation of both $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ during the deactivation of T_1 by O_2 and the measurement of the 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 $O_2(^3\Sigma_g^-)$ formation became possible.[22,23]

In our following investigations we realized that quenching of T_1 by O_2 occurs via two different deactivation channels.[24−27] We determined rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ for 13 triplet sensitizers of very different E_T,[24] for 9 naphthalene derivatives (NDs),[25,26] and for 10 biphenyl derivatives (BDs),[27] whereby in both series of $\pi\pi^*$ triplet sensitizers E_{ox} strongly varies at almost constant E_T. In accordance with the literature, it was assumed that $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ are formed by competitive internal conversion (ic) of excited complexes $^m(T_1{\cdot}^3\Sigma)$ of multiplicity $m = 1$ and 3 to lower complex states and subsequent dissociation into ground-state sensitizer S_0 and O_2 in the respective product state, i.e., by ic $^1(T_1{\cdot}^3\Sigma) \rightarrow {}^1(S_0{\cdot}^1\Sigma)$, $^1(T_1{\cdot}^3\Sigma) \rightarrow {}^1(S_0{\cdot}^1\Delta)$, and $^3(T_1{\cdot}^3\Sigma) \rightarrow {}^3(S_0{\cdot}^3\Sigma)$. The analysis of the large set of novel data from $\pi\pi^*$ triplet sensitizers unequivocally revealed that ic originates from $^{1,3}(T_1{\cdot}^3\Sigma)$ excited complexes without particular charge transfer (CT) interactions (nCT complexes), i.e., encounter complexes, and for sensitizers of low oxidation potential additionally from $^{1,3}(T_1{\cdot}^3\Sigma)$ complexes with partial CT character (pCT complexes), i.e., exciplexes.[26,27] Competitive ic to complexes of lower energy is the rate determining event in the nCT channel. The corresponding rate constants depend on the respective excess energies ΔE ($\Delta E_{1\Sigma} = E_T - E_\Sigma$, $\Delta E_{1\Delta} = E_T - E_\Delta$, $\Delta E_{3\Sigma} = E_T$) and follow a common energy gap law for $\pi\pi^*$ triplet sensitizers. The respective rate

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10.1021/jp013363+ CCC: $22.00

constants of the pCT channel vary on a logarithmic scale approximately linearly with the free energy change ΔG_{CET} for complete electron transfer from T_1 excited sensitizer to O_2. The statistical weights of the pCT processes leading to singlet and ground state oxygen behave like 1:3 in accordance with the spin-statistical weight ratio. However, a fully established intersystem crossing (isc) equilibrium $^1(T_1{\cdot}^3\Sigma) \rightleftharpoons {}^3(T_1{\cdot}^3\Sigma)$ could surprisingly only be proven for encounter complexes but not for exciplexes.[26,27]

The influence of the electronic configuration ($\pi\pi^*$ vs $n\pi^*$) on the rate constants of T_1 state quenching by O_2 and on the efficiencies S_Δ of $O_2(^1\Delta_g)$ generation is still less well understood.[28−37] Although exceptions are known,[28−30] S_Δ values are generally found to be significantly lower with $n\pi^*$ triplet states ($S_\Delta \approx 0.3-0.5$) than with $\pi\pi^*$ triplet states ($S_\Delta \approx 0.8-1.0$).[24,32−36] Different features of the investigated $n\pi^*$ triplets have been evoked to explain this behavior, such as their high polarizability[33] or large Franck−Condon factors for the deactivation of ketone−oxygen complexes.[34] In our study on 13 triplet sensitizers of very different E_T, we noticed an apparently anomalous behavior of the only two $T_1(n\pi^*)$ sensitizers benzophenone and acetophenone with respect to the rate constants $k_T^{1\Delta}$. The corresponding values have been found by about 1 order of magnitude larger than those expected on the common energy gap relation found for the $T_1(\pi\pi^*)$ sensitizers.[24] We speculated that in the $^1(T_1(n\pi^*){\cdot}^3\Sigma) \rightarrow {}^1(S_0(n^2){\cdot}^1\Delta)$ transition, possibly the concomitant one-center orbital jump of the electron in the $n\pi^* \rightarrow n^2$ transition at the ketone O atom couples to the simultaneous change of the orbital angular momentum accompanying the $^3\Sigma \rightarrow {}^1\Delta$ transition of O_2, thus promoting this transition compared with the $^1(T_1(n\pi^*){\cdot}^3\Sigma) \rightarrow {}^1(S_0(n^2){\cdot}^1\Sigma)$ transition and with the $^1(T_1(\pi\pi^*){\cdot}^3\Sigma) \rightarrow {}^1(S_0(\pi^2){\cdot}^1\Delta)$ and $^1(T_1(\pi\pi^*){\cdot}^3\Sigma) \rightarrow {}^1(S_0(\pi^2){\cdot}^1\Sigma)$ transitions of $T_1(\pi\pi^*)$ sensitizers. Such a promoting effect was already found to cause the increase in the rate of $n\pi^* \rightarrow n^2$ isc compared with $\pi\pi^* \rightarrow \pi^2$ isc.[38,39]

The determination of the efficiency ratio a/S_Δ for a series of benzophenones and acetophenones by Wang and Ogilby seemed to support our speculation.[37] However, a systematic study of the influence of the electronic configuration on the rate constants of the processes leading to $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ formation in the T_1 state quenching by O_2 with sensitizers of known E_{ox} is still lacking. Therefore, we decided to investigate a number of $T_1(n\pi^*)$ sensitizers using the new method of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ determination. The benefits of studying series of structurally closely related sensitizers varying only one principal molecular parameter have already been demonstrated.[14,17−19,26,27,31,34] We investigated the triplet-state quenching by O_2 of differently substituted benzophenones (BPs), which is particularly advantageous because of the following reasons: (i) the T_1 state configuration of BP of *para*-halogen- and *para*-methoxysubstituted BPs is undoubtedly $n\pi^*$ in nonpolar solvents;[40] (ii) previously observed correlations of the rate constants of T_1 state quenching of BPs by O_2 with Hammett σ^+ values and E_{ox} indicate that exciplex formation actually occurs during this process;[31,41] (iii) substitution has very little effect on E_T but induces large changes in the oxidation potential of BPs; (iv) BPs differ from BDs only by the central carbonyl group, and hence, a comparison with the results obtained with this structurally similar series of $T_1(\pi\pi^*)$ sensitizers will be most informative.

Experimental Details

CCl_4 (TET, Merck, p.a., Al_2O_3) and phenalenone (PHE, Aldrich, 97%, silica gel/CH_2Cl_2) were purified by column chromatography. Benzene (Aldrich, 99+%) and erythrosin B (Aldrich, 95%) were used as received. 4,4′-Dimethoxybenzophenone (DMOBP, Lancaster, 98+%), 4-methoxybenzophenone (MOBP, Aldrich, 97%), 3,4-dimethylbenzophenone (DMEBP, Aldrich, 99%), 4-methylbenzophenone (MEBP, Aldrich, 99%), benzophenone (BP, Aldrich, 99+%), 4-bromobenzophenone (BrBP, Aldrich, 98%), 4-chlorobenzophenone (ClBP, Aldrich, 99%), 4,4′-dichlorobenzophenone (DClBP, Lancaster, 99%), 4-trifluoromethylbenzophenone (TFMBP, Lancaster, 98%), and 4-cyanobenzophenone (CNBP, Lancaster, 98%) were recrystallized from *n*-hexane. The solutions were prepared and filled into sample cells in a glovebox under dry atmosphere to avoid uptake of humidity in the investigation of $O_2(^1\Sigma_g^+)$. The determination of the quantum yields of $O_2(^1\Sigma_g^+)$ singlet oxygen and of overall ($O_2(^1\Sigma_g^+) + O_2(^1\Delta_g)$) singlet oxygen sensitization have already been described in detail in previous papers.[22,24] Triplet-state lifetimes in deoxygenated (O_2 removal by Ar bubbling) and in air-saturated TET have been measured monitoring the respective sensitizer phosphorescence. The equipment has been very much improved since the early measurements and is already described.[25] Quenching experiments were carried out in air-saturated TET at room temperature with $[O_2] = 2.3 \times 10^{-3}$ M, calculated from $[O_2] = 1.24 \times 10^{-2}$ M given for the O_2 partial pressure 1 bar,[42] considering the TET vapor pressure of 0.126 bar. Four independent series of comparative experiments with reference sensitizer PHE ($a = 0.60$, $S_\Delta = 0.97$)[24,43] have been performed with each sensitizer, varying the laser pulse energy. Only energy independent results are reported.

Results

The triplet-state lifetime τ_T is in oxygen free solutions much shorter for $n\pi^*$ than for $\pi\pi^*$ triplet states due to enhanced $n\pi^* \rightarrow n^2$ isc.[38,39] Thus, the common assumption that T_1 is already completely quenched at $[O_2] \approx (1-2) \times 10^{-3}$ M, which is typical for air-saturated solutions, is not valid for the BPs. Therefore, determination of τ_T and of the triplet-state lifetime τ_T^{O2} in air-saturated solution is necessary for the calculation of the efficiency f_T^{O2} of T_1 state quenching by O_2, which is given by eq 1:

$$f_T^{O_2} = 1 - \tau_T^{O_2}/\tau_T \qquad (1)$$

Table 1 lists the lifetimes τ_T which range between 1 and 10 μs and the values of τ_T^{O2} which continuously decrease from CNBP with 670 ns to DMOBP with 120 ns, i.e., from the BP with strongest electron withdrawing substituent to the BP with the strongest electron electron donating substituents. This already qualitatively indicates that CT interactions contribute to the enhancement of T_1 state quenching by O_2, in accordance with the results of Chattopadhyay et al.[31]

The experimentally determined quantum yields of $O_2(^1\Sigma_g^+)$ singlet oxygen and of overall ($O_2(^1\Sigma_g^+) + O_2(^1\Delta_g)$) singlet oxygen sensitization are $Q_\Sigma = Q_T f_T^{O_2} a$ and $Q_\Delta = Q_T f_T^{O_2} S_\Delta$, respectively, where Q_T is the isc quantum yield which amounts to unity for aromatic $n\pi^*$ ketones.[42] Thus, we obtain the efficiencies a and S_Δ of Table 1 as $a = Q_\Sigma/f_T^{O_2}$ and $S_\Delta = Q_\Delta/f_T^{O_2}$, which are between 5 and 15% larger than the corresponding quantum yields. The substituent effect on the efficiencies a and S_Δ is much weaker than on $\tau_T^{O_2}$. Both decrease only moderately when going from CNBP to DMOBP. We also calculated relative efficiency ratios $a/S_{\Delta,r}$ normalized to the value for benzophenone for a comparison with the data of Wang and Ogilby in the last column of Table 1.[37] We obtain a similar graduation if the mutual uncertainties are taken into account.

TABLE 1: Triplet-State Lifetimes and Efficiencies of Singlet Oxygen Sensitization

sensitizer	$\tau_T{}^a$ (10^{-6} s)	$\tau_T{}^{O_2\,b}$ (10^{-7} s)	$f_T{}^{O_2\,c}$	$Q_\Delta{}^d$	$Q_\Sigma{}^e$	$S_\Delta{}^d$	a^e	$a/S_{\Delta,r}{}^f$	$a/S_{\Delta,r}{}^g$
TFMBP	8.45	3.81	0.955	0.473	0.301	0.495	0.315	1.64	1.50
CNBP	9.75	6.67	0.932	0.501	0.317	0.538	0.340	1.63	1.80
DClBP	4.38	3.84	0.912	0.439	0.278	0.481	0.305	1.63	1.20
ClBP	4.31	3.04	0.930	0.423	0.200	0.455	0.215	1.22	1.05
BrBP	1.95	2.97	0.848	0.419	0.230	0.494	0.271	1.41	1.05
BP	9.00	2.50	0.972	0.438	0.170	0.451	0.175	1.00	1.00
MBP	3.33	2.28	0.932	0.409	0.162	0.439	0.174	1.02	1.00
DMBP	3.04	2.29	0.925	0.397	0.183	0.429	0.198	1.19	1.10
MOBP	2.47	1.47	0.940	0.362	0.184	0.385	0.196	1.31	–
DMOBP	1.18	1.16	0.902	0.327	0.178	0.362	0.197	1.40	–

[a] ±15%. [b] ±10%. [c] ±2%. [d] ±5%. [e] ±12%. [f] ±13%. [g] Relative ratios $a/S_{\Delta,r}$ normalized to the BP value, ref 37.

TABLE 2: Rate Constants of Quenching and of Product Formation

sensitizer	$k_T{}^{Q\,a}$ (10^{-9} M^{-1} s^{-1})	$k_D{}^a$ (10^{-9} s^{-1})	$k_T{}^{1\Sigma\,b}$ (10^{-9} s^{-1})	$k_T{}^{1\Delta}$ (10^{-9} s^{-1})	dx/x^c	$k_T{}^{3\Sigma\,d}$ (10^{-9} s^{-1})
TFMBP	1.09	1.14	0.36	0.20	0.27	0.57
CNBP	0.61	0.62	0.21	0.12	0.27	0.29
DClBP	1.03	1.07	0.33	0.19	0.28	0.56
ClBP	1.33	1.40	0.30	0.34	0.18	0.76
BrBP	1.24	1.30	0.35	0.29	0.23	0.66
BP	1.69	1.80	0.32	0.50	0.15	0.99
MBP	1.78	1.90	0.33	0.50	0.16	1.07
DMBP	1.76	1.88	0.37	0.44	0.18	1.07
MOBP	2.78	3.10	0.61	0.59	0.19	1.91
DMOBP	3.40	3.88	0.77	0.64	0.22	2.47

[a] ±10%. [b] ±16%. [c] dx/x is the relative uncertainty of $k_T{}^{1\Delta}$. [d] ±12%.

The primary data of Table 1 allow the evaluation of the rate constants of the processes leading to the 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. Equation 2 is used for the calculation of the overall quenching rate constant $k_T{}^Q$:

$$k_T{}^Q = (1/\tau_T{}^{O2} - 1/\tau_T)/[O_2] \qquad (2)$$

Values of $k_T{}^Q$ are listed in Table 2. They increase by a factor of 6 from CNBP to DMOBP. The maximum value of 3.4×10^9 M^{-1} s^{-1} is still by the factor 8 smaller than the 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 TET.[44]

In the first step of quenching, $^{1,3,5}(T_1{\cdot}^3\Sigma)$ encounter complexes of T_1 excited sensitizer and $O_2(^3\Sigma_g{}^-)$ are formed. We have recently shown that a fast isc equilibrium $^1(T_1{\cdot}^3\Sigma) \rightleftharpoons {}^3(T_1{\cdot}^3\Sigma)$ between these encounter complexes is established, from which ic to lower complex states occurs. This equilibrium may even be fed for sensitizers with very low oxidation potential by quintet exciplexes, which have no own product channel.[26,27] It is therefore reasonable to evaluate the overall rate constant k_D of the deactivation of nCT complexes $^{1,3,5}(T_1{\cdot}^3\Sigma)$ by eq 3, 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 overall rate constant k_D to the products ground-state sensitizer S_0 and $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$:

$$k_D = k_{-diff} d_T{}^Q/(k_{diff} - k_T{}^Q) \qquad (3)$$

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.[11] A smaller value of g would lead to proportionally smaller absolute values of k_D (see eq 3). 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 $k_T{}^{3\Sigma} = (1 - S_\Delta)k_D$. The results are listed in Table 2.

We observe graduated increases of the rate constants in going from CNBP to DMOBP, i.e., with increasing CT interaction, by factors of 3.5 for $k_T{}^{1\Sigma}$, of 5 for $k_T{}^{1\Delta}$ and of 8 for $k_T{}^{3\Sigma}$. 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 can be calculated by eq 4, originally derived by Rehm and Weller[45,46]

$$\Delta G_{CET} = F(E_{ox} - E_{red}) - E_T + C \qquad (4)$$

F and E_{red} represent Faraday's constant and the reduction potential of the electron acceptor (for O_2 −0.78 V vs SCE),[47] and C is the electrostatic interaction energy. The term C is definitely positive in nonpolar solvents.[48] However, since we will discuss rate constants determined only in one solvent, a shifted scale of ΔG_{CET} values obtained with $C = 0$ is already sufficient. Oxidation potentials measured for BP and several electron rich BPs versus Ag/AgCl reference electrode in acetonitrile with tetrabutylammoniumhexafluorophosphate as supporting electrolyte are listed in Table 3.[41]

No oxidation peaks were observed with the halogenated BPs and CNBP. However, an estimation of their E_{ox} values can be easily obtained. Substituent effects on the oxidation potentials of several aromatic compounds were shown to give excellent correlations with Hammett σ values.[49,50] This implies a correlation between the oxidation potentials of these series of compounds, according to the substituent. Such a correlation is actually observed with the E_{ox} data of the BPs (V vs Ag/AgCl) and the E_{ox} data of the BDs (V vs SCE).[18] The data of Table 3 yield the relationship E_{ox}(BP, V vs Ag/AgCl) = 0.70 + 1.07 E_{ox}(V vs SCE), which is used to estimate the oxidation potentials of the BPs. The combination of E_{ox}(BP, V vs Ag/AgCl) with

TABLE 3: Quantities for the Estimation of the Free Energy Change ΔG_{CET} for Complete Electron Transfer from the T_1 Excited Benzophenone to O_2

biphenyl	E_{ox}[a] (V vs SCE)	ketone	E_{ox}[b] (V vs Ag/AgCl)	E_{ox}[c] (V vs Ag/AgCl)	E_T (kJ mol^{-1})	ΔG_{CET}[d] (kJ mol^{-1})
4-cyanobiphenyl	2.11	CNBP		2.96	279	77.6
4,4-dichlorobiphenyl	2.02	DClBP		2.86	286	61.3
4-chlorobiphenyl	1.96	ClBP		2.80	287	54.1
4-bromobiphenyl	1.95	BrBP		2.78	289	51.1
biphenyl	1.91	BP	2.85	2.74	287	49.0
4-methylbiphenyl	1.80	MBP	2.60	2.62	289	35.6
4,4-dimethylbiphenyl	1.69	DMBP	2.45	2.51	287	26.3
4-methoxybiphenyl	1.53	MOBP	2.20	2.34	290	6.8
4,4-dimethoxybiphenyl	1.30	DMOBP	2.20	2.09	293	−19.9

[a] Ref 18. [b] Ref 41. [c] Estimated by the correlation E_{ox}(BP, V vs Ag/AgCl) = 0.70 + 1.07E_{ox}(BD, V vs SCE); subtracting 0.09 V yields E_{ox}(BP, V vs SCE), as shown in ref 41. [d] Relative scale of ΔG_{CET} values calculated by eq 3 with $C = 0$.

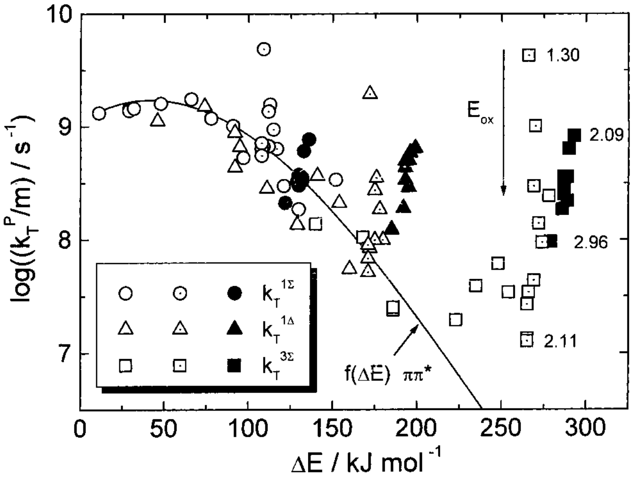


Figure 1. Dependence of log(k_T^P/m) on the excess energy ΔE of the different deactivation channels. Data of the $T_1(\pi\pi^*)$ sensitizers of ref 24 as open symbols; data of the $T_1(\pi\pi^*)$ BDs as symbols with dot.[27] Data of the $T_1(n\pi^*)$ benzophenones as full symbols. The numbers indicate the variation of E_{ox} of BDs and BPs.

E_{red} (O_2, V vs SCE) in eq 4 leads to an additional shift of ΔG_{CET}, which, however, is not important in the following discussion.

Discussion

The interplay between non-CT and CT mechanisms in the quenching of T_1 states by O_2 is best illustrated by Figure 1, which 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 ΔE for all $T_1(\pi\pi^*)$ sensitizers of our first study on the triplet-state energy dependence of the T_1 quenching by O_2 (open symbols)[24,51] and for the BDs (symbols with dot center).[27] The data of the NDs, which show a very similar behavior like the BD data,[26] have been omitted to preserve clarity of the representation.

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 ΔE for $\Delta E \leq 220$ kJ mol^{-1}. This common dependence is the result of the competition of ic processes originating from excited complexes $^{1,3}(T_1{\cdot}^3\Sigma)$. Kawaoka et al. derived eq 4 for the rate constant k_{ic} of ic of a weakly bound exciplex[52]

$$k_{ic} = (4\pi^2/h)\rho(\Delta E)F(\Delta E)\beta^2 \qquad (5)$$

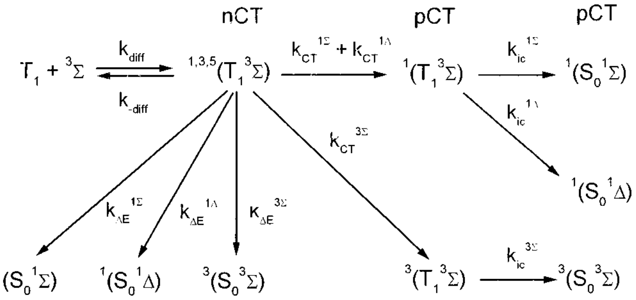
Here, $\rho(\Delta E)$ is the density of final states which are nearly degenerate with the initial state, ΔE is the excess energy, $F(\Delta E)$ is the Franck−Condon Factor, and β is the electronic coupling matrix element. The product $F'(\Delta E) = \rho(\Delta E)F(\Delta E)$ is the Franck−Condon weighted density of states which decreases with increasing ΔE at higher excess energies. The rate constants of ic and consequently also the multiplicity-normalized rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $3k_T^{3\Sigma}/3$ should depend in a common way on ΔE as long as (i) 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, (ii) the equilibrium between the singlet and triplet excited complexes $^{1,3}(T_1{\cdot}^3\Sigma)$ is fully established, and (iii) no other mechanisms become important. This is what actually can be seen in Figure 1 with the open symbols for $\Delta E \leq 220$ kJ mol^{-1}. The dependence of these data of log(k_T^P/m) on ΔE is described by the empirical curve $f(\Delta E)$ of Figure 1,[53] which declines much weaker than Siebrand's energy gap law,[54−56] since it reflects the energy gap law for complexes $^{1,3}(T_1{\cdot}^3\Sigma)$ with only very small binding interactions.

In the region of triplet-state energies $E_T \geq 230$ kJ mol^{-1} an additional CT mechanism becomes important, leading to a strong increase of log($k_T^{3\Sigma}/3$) with $\Delta E_{3\Sigma} = E_T$, see the open symbols of Figure 1. It is known that CT interactions mainly depend on two molecular parameters, triplet-state energy and oxidation potential. The influence of CT interactions is clearly demonstrated for the series of BDs (symbols with dot center) with almost constant E_T but strongly varying E_{ox}. With decreasing E_{ox}, one observes a graduated increase of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}/3$. The variation increases from 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 deactivation mechanism operates, which takes place via complexes $^{1,3}(T_1{\cdot}^3\Sigma)$ with partial CT character, i.e., via exciplexes.

We noted already earlier that the logarithms of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}/3$ of the NDs with large E_{ox}, i.e., with small or negligible CT interactions, are near the empirical curve f(ΔE).[26] This also holds true for the log($k_T^{1\Sigma}$) and log($k_T^{1\Delta}$) data of the BDs, clearly indicating 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 $^{1,3}(T_1{\cdot}^3\Sigma)$ complexes with no CT character (nCT complexes), which we cannot distinguish from encounter complexes. Thus, Figure 1 impressively demonstrates that two mechanisms additionally 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, the other by the strength of CT interactions. The first occurs via excited nCT complexes and the second via exciplexes with partial CT character (pCT).

The results of these studies on the $T_1(\pi\pi^*)$ sensitizers are summarized in the kinetic Scheme 1, which also will be used for the analysis of the data of the $T_1(n\pi^*)$ BPs.[24,26,27] In the primary step, $^{1,3,5}(T_1{\cdot}^3\Sigma)$ nCT complexes are formed. The isc equilibrium between the complexes $^{1,3}(T_1{\cdot}^3\Sigma)$ nCT complexes is fully established. These complexes decay by ic to nCT

SCHEME 1

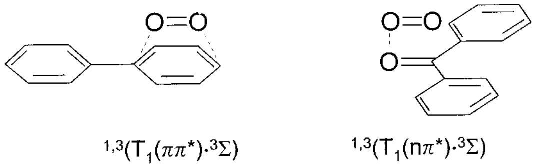


complex states of lower energy which finally dissociate to yield ground-state sensitizer S_0 and $O_2({}^1\Sigma_g{}^+)$, $O_2({}^1\Delta_g)$, or $O_2({}^3\Sigma_g{}^-)$. The competing ic is the rate determining step of deactivation in the nCT channel. The respective multiplicity normalized rate constants $k_{\Delta E}{}^{1\Sigma}$, $k_{\Delta E}{}^{1\Delta}$, and $k_{\Delta E}{}^{3\Sigma}/3$ follow a common energy gap law. With increasing CT interactions between $T_1(\pi\pi^*)$ and O_2, i.e., with increasing E_T and/or decreasing E_{ox}, the formation of ${}^{1,3}(T_1{\cdot}{}^3\Sigma)$ pCT complexes begins to compete with the ic of ${}^{1,3}(T_1{\cdot}{}^3\Sigma)$ nCT complexes. This reaction is the rate determining step of the pCT deactivation channel and transfers the spin statistical weight of 1:3 to the ${}^{1,3}(T_1{\cdot}{}^3\Sigma)$ exciplexes. The corresponding rate constants $k_{CT}{}^{1\Sigma}$, $k_{CT}{}^{1\Delta}$, and $k_{CT}{}^{3\Sigma}/3$ depend in the same exponential way on ΔG_{CET}. Subsequent ic is apparently fast and proceeds with rate constants $k_{ic}{}^{1\Sigma}$, $k_{ic}{}^{1\Delta}$, and $k_{ic}{}^{3\Sigma}$ to produce finally ground-state sensitizer S_0 and $O_2({}^1\Sigma_g{}^+)$, $O_2({}^1\Delta_g)$, or $O_2({}^3\Sigma_g{}^-)$ via the pCT channel. The overall rate constants of ${}^{1,3,5}(T_1{\cdot}{}^3\Sigma)$ nCT complex deactivation $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$ are thus each additively composed of the corresponding rate constants $k_{\Delta E}{}^{1\Sigma}$, $k_{\Delta E}{}^{1\Delta}$, $k_{\Delta E}{}^{3\Sigma}$ and $k_{CT}{}^{1\Sigma}$, $k_{CT}{}^{1\Delta}$, $k_{CT}{}^{3\Sigma}$, reproducing quantitatively the contributions of non-CT and CT interactions in the deactivation of $T_1(\pi\pi^*)$ states by O_2.[26,27]

The data of the $T_1(n\pi^*)$ BP sensitizers which are also displayed in Figure 1 reveal a surprisingly different behavior compared with the BDs. It is true that the $\log(k_T{}^P/m)$ data also decrease with increasing E_{ox} at nearly constant E_T; however, there are several significant differences: (i) despite of the large variation of E_{ox} (2.09 to 2.96 vs Ag/AgCl for the BPs, 1.30 to 2.11 V vs SCE for the BDs) and their even larger mean E_T (287 vs. 268 kJ mol^{-1}), a much smaller variation of the rate constants of the BPs with E_{ox} has to be noted; (ii) the graduation increases only weakly with increasing ΔE; (iii) $\log(k_T{}^{1\Sigma})$, $\log(k_T{}^{1\Delta})$, and $\log(k_T{}^{3\Sigma}/3)$ are of similar magnitude for each BP sensitizer; (iv) the $\log(k_T{}^P/m)$ data of the BPs with the highest E_{ox}, for which only very small CT interactions can take place, are in part far apart from the empirical curve $f(\Delta E)$ found for $T_1(\pi\pi^*)$ sensitizers.

This surprisingly different behavior is caused by the different electronic and, in consequence, sterical structure of the intermediate ${}^{1,3}(T_1{\cdot}{}^3\Sigma)$ complexes of the BPs. In comparative investigations of the CT induced quenching processes of T_1 states by triplet ground-state O_2 and of $O_2({}^1\Delta_g)$ by singlet ground-state sensitizers S_0, we recently discovered that both proceed via a common pCT deactivation channel.[57,58] A common pCT channel means that the CT induced deactivation passes $(T_1{\cdot}{}^3\Sigma)$ or $(S_0{\cdot}{}^1\Delta)$ complexes of the same partial charge-transfer character and structure. This was found for the NDs as well as for the BDs.[57,58] Significant information on the nature of the intermediate $(S_0{\cdot}{}^1\Delta)$ pCT structures formed with aromatic compounds is available from chemical reactions of $O_2({}^1\Delta_g)$ with aromatic compounds and from ab initio calculations.[59,60] A CT intermediate concerning one ring of a ND is suggested by the chemical reactivity of 1,4-dimethylnaphthalene, which yields a 1,4-endoperoxide upon addition of singlet oxygen.[59] In a recent MCSCF study by Bobrowski et al.,[60] it was shown that unsubstituted benzene rings are able to provide a supra−supra CT transition structure with singlet oxygen. Thus, there is sufficent evidence that structures, where the oxygen atoms of O_2 interacts with two opposite carbon atoms of an aromatic ring, correspond to $(T_1(\pi\pi^*){\cdot}{}^3\Sigma)$ and $(S_0(\pi^2){\cdot}{}^1\Delta)$ pCT complexes, at least for NDs and BDs (see Scheme 2). It is most remarkable that for BPs no common pCT deactivation channel was found.[41] It is true that the correlation of rate constants of CT induced $O_2({}^1\Delta_g)$ quenching by ground-state BPs of very low E_{ox} versus ΔG_{CET} is very similar to the corresponding correlation of the BDs; however, the data of the rate constants of CT induced quenching of $T_1(n\pi^*)$ BPs by O_2 are far apart from the corresponding correlation of the $T_1(\pi\pi^*)$ BDs and NDs. From this result, we concluded that the $(S_0(n^2){\cdot}{}^1\Delta)$ pCT complexes formed in the reaction of S_0 state BP and $O_2({}^1\Delta_g)$ are also of supra−supra structure, where O_2 interacts with one aromatic ring. But this does not hold true for the $(T_1(n\pi^*){\cdot}{}^3\Sigma)$ pCT complexes. Since the excitation of the $T_1(n\pi^*)$ of BPs state is localized on the carbonyl group, a four-center structure, where O_2 is in parallel arrangement to the CO group, is of course much more probable for $(T_1(n\pi^*){\cdot}{}^3\Sigma)$ pCT complexes than a supra−supra structure which is realized with the delocalized excitation of the $(T_1(\pi\pi^*){\cdot}{}^3\Sigma)$ pCT complex of BDs (see Scheme 2).[41] These results are of eminent importance for the interpretation of the present results of the BPs.

SCHEME 2



It can be assumed that deactivation of ${}^{1,3}(T_1{\cdot}{}^3\Sigma)$ complexes by ic occurs with conservation of the molecular structure, i.e., either supra-supra structure or four-center structure, to complexes ${}^1(S_0{\cdot}{}^1\Sigma)$, ${}^1(S_0{\cdot}{}^1\Delta)$, or ${}^3(S_0{\cdot}{}^3\Sigma)$. Since the O−O bond varies only slightly between 1.21 (${}^3\Sigma$), 1.22 (${}^1\Delta$), and 1.23 Å (${}^1\Sigma$)[61] and since only small changes of bond lengths take place in the $\pi\pi^* \rightarrow \pi^2$ deactivation of the aromatic moiety, correspondingly small structural changes can be expected in the ic of supra-supra ${}^{1,3}(T_1(\pi\pi^*){\cdot}{}^3\Sigma)$ complexes. This is the reason the empirical curve $f(\Delta E)$ found for $T_1(\pi\pi^*)$ sensitizers, reflecting the excess energy dependence of $\log(F'(\Delta E))$, is still comparatively steep. In contrast, much larger changes have to be expected for the ic of four-center ${}^{1,3}(T_1(n\pi^*){\cdot}{}^3\Sigma)$ complexes. It is well-known that significant changes of the lengths of all three bonds of the carbonyl carbon atom of BPs occur during $n\pi^* \rightarrow n^2$ deexcitation.[62] Therefore, the deactivation of ${}^{1,3}(T_1(n\pi^*){\cdot}{}^3\Sigma)$ complexes is qualitatively best described by displaced potential energy curves of upper and lower states, which correspond to a weaker excess energy dependence of $\log(F'(\Delta E))$. The dependence of $\log(k_T{}^P/m)$ on ΔE observed for CNBP ($E_{ox} = 2.96$ V vs Ag/AgCl), for which minimal CT interactions can be reasonably assumed, could be taken as a rough approach to the function $f(\Delta E)$ describing the excess energy dependence of ic of ${}^{1,3}(T_1(n\pi^*){\cdot}{}^3\Sigma)$ complexes. This function is by way of trial drawn as straight line in Figure 2 and displays actually the much weaker excess energy dependence expected. Thus, we conclude that the principal reason for the different dependence of $\log(k_T{}^P/m)$ on ΔE is the significant change of bond lengths in the four-center complex structure during ic of ${}^{1,3}(T_1(n\pi^*){\cdot}{}^3\Sigma)$ complexes.

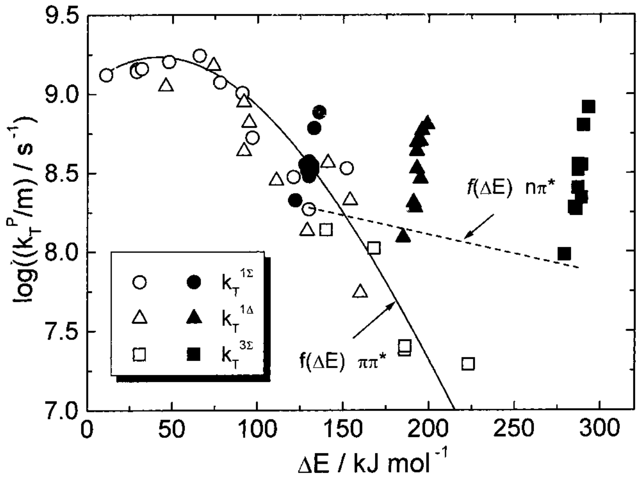


Figure 2. Dependence of $\log(k_T{}^P/m)$ on the excess energy ΔE of the different deactivation channels. Data of the $T_1(\pi\pi^*)$ sensitizers of ref 24 for $\Delta E \leq 220$ kJ mol^{-1} as open symbols. Data of the $T_1(n\pi^*)$ benzophenones as full symbols. The solid line represents the function $f(\Delta E)$ for $T_1(\pi\pi^*)$ sensitizers and the dotted line the estimate $f(\Delta E)$ for $T_1(n\pi^*)$; see text.

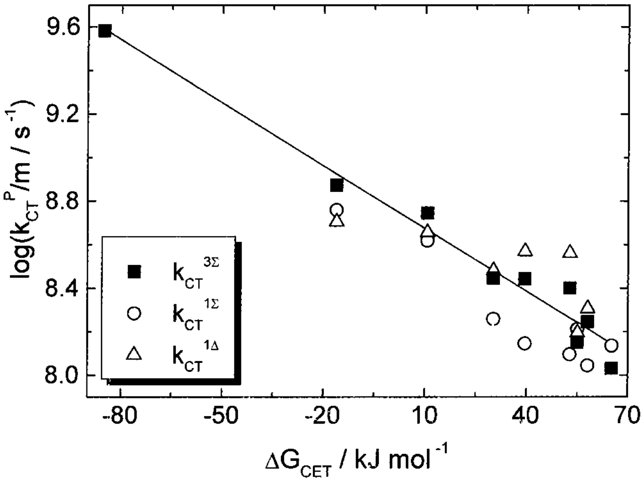


Figure 3. Dependence of $\log(k_{CT}{}^P/m)$ on the change of free energy ΔG_{CET} for complete electron transfer from $T_1(n\pi^*)$ excited BPs to O_2. Straight line with slope -0.0096 ± 0.0006 mol kJ^{-1} and intercept 8.77 ± 0.09 results from the linear fit to the $\log(k_{CT}{}^{3\Sigma}/3)$ data.

The straight line $f(\Delta E) = 8.60 - 0.00246\Delta E$ of Figure 2 is used to estimate the values of $k_{\Delta E}{}^{1\Sigma}$, $k_{\Delta E}{}^{1\Delta}$, and $k_{\Delta E}{}^{3\Sigma}/3$ for the $T_1(n\pi^*)$ ketones. With the average triplet-state energy $E_T = 287$ kJ mol^{-1} of the BPs and the resulting excess energies $\Delta E_{1\Sigma} = 130$, $\Delta E_{1\Delta} = 193$, and $\Delta E_{3\Sigma} = 287$ kJ mol^{-1}, we obtain $k_{\Delta E}{}^{1\Sigma} = 1.9 \times 10^8$, $k_{\Delta E}{}^{1\Delta} = 1.3 \times 10^8$, and $k_{\Delta E}{}^{3\Sigma}/3 = 7.8 \times 10^7$ 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 BP sensitizer the rate constants $k_{CT}{}^{1\Sigma}$, $k_{CT}{}^{1\Delta}$, and $k_{CT}{}^{3\Sigma}/3$ of CT 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 uncertainties of these differences strongly increase with increasing E_{ox} and are larger for $k_{CT}{}^{1\Sigma}$ and $k_{CT}{}^{1\Delta}$ than for $k_{CT}{}^{3\Sigma}/3$ because of the smaller CT effects. Figure 3 displays all values of $\log(k_{CT}{}^P/m)$ for differences larger than 8×10^7 s^{-1}, together with $\log(k_{CT}{}^{3\Sigma}/3)$ determined for 4-aminobenzophenone (AMBP) in a plot of $\log(k_{CT}{}^P/m)$ versus ΔG_{CET}.[41,63]

The data of $\log(k_{CT}{}^{3\Sigma}/3)$, correlate linearly with ΔG_{CET}. The least-squares fit results in the straight line $f(\Delta G_{CET}) = 8.77 - 0.0096\Delta G_{CET}$ shown in Figure 3. If the value of AMBP is omitted, almost the same slope and intercept are obtained ($8.74 - 0.0098\Delta G_{CET}$), indicating that the correlation extends over a wide ΔG_{CET} range. Only small changes in the plot $\log(k_{CT}{}^P/m)$ versus ΔG_{CET} are observed if a steeper declining function for the excess energy dependence of $\log(F'(\Delta E))$ for the ic of $^{1,3}(T_1(n\pi^*){\cdot}^3\Sigma)$ nCT complexes is used. The data of $\log(k_{CT}{}^{1\Sigma})$ and $\log(k_{CT}{}^{1\Delta})$ correlate with apparently similar strength with ΔG_{CET}. The corresponding linear correlation yielded $f(\Delta G_{CET}) = 7.45 - 0.033\Delta G_{CET}$ for the BD $T_1(\pi\pi^*)$ sensitizers. Thus, the slope obtained with the $T_1(n\pi^*)$ BP sensitizers is smaller by a factor of 3 than that obtained with the $T_1(\pi\pi^*)$ sensitizers, pointing to significantly weaker CT interactions in $^{1,3}(T_1(n\pi^*){\cdot}^3\Sigma)$ pCT complexes. This result is not very surprising if it is considered that the effect of electron donating or electron withdrawing substituents is only large if they are directly bound to the reaction center, which is the case for the supra−supra structure of the $^{1,3}(T_1(\pi\pi^*){\cdot}^3\Sigma)$ pCT complexes of the BDs but not for the four-center structure of the locally excited $^{1,3}(T_1(n\pi^*){\cdot}^3\Sigma)$ pCT complexes of the BPs.

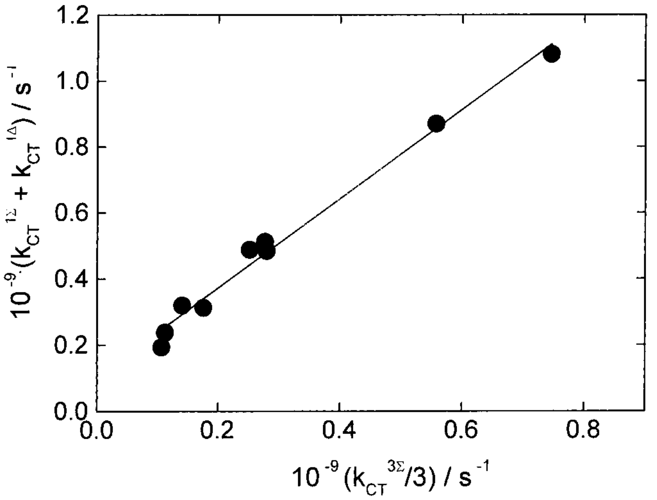


Figure 4. Correlation of $k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta}$ with $k_{CT}{}^{3\Sigma}/3$ for BPs. Linear least-squares fit results in slope 1.35 ± 0.06 and intercept $(1.0 \pm 0.4) \times 10^8$ s^{-1}.

The scatter of the $\log(k_{CT}{}^{1\Sigma})$ and $\log(k_{CT}{}^{1\Delta})$ data is somewhat larger than for the $\log(k_{CT}{}^{3\Sigma}/3)$ data of Figure 3, 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 $f(\Delta G_{CET})$. It appears that $k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta} \approx k_{CT}{}^{3\Sigma}/3$ can hold true in the series of BPs, which would be equivalent to the weight ratio 1:3 for the efficiencies of deactivation through the singlet and triplet pCT channels, in accordance with the spin-statistical ratio. This was exactly found for the BDs and indicates, if a graduation of ic rate constants according to the respective excess energies similarly to the nCT channel is also valid for the pCT channel, (i) the formation of the pCT complexes but not their decay by ic as the rate determining step of the pCT channel and (ii) a much faster ic of $^{1,3}(T_1{\cdot}^3\Sigma)$ pCT complexes than the isc between singlet and triplet $^{1,3}(T_1{\cdot}^3\Sigma)$ pCT complexes.[27] However, this ratio is not exactly verified by Figure 4, in which the correlation $k_{CT}{}^{1\Sigma} + k_{CT}{}^{1\Delta}$ versus $k_{CT}{}^{3\Sigma}/3$ leads to a straight line with slope 1.35 instead of unity.

If this moderate deviation should be significant, then the larger than spin-statistical weight of the singlet pCT channel could be understood as the result of isc processes, which are not much slower than the ic of the $^{1,3}(T_1{\cdot}^3\Sigma)$ pCT complexes. Then, the larger rate constants of ic to $^1(S_0{\cdot}^1\Sigma)$ and $^1(S_0{\cdot}^1\Delta)$ compared with ic to $^3(S_0{\cdot}^3\Sigma)$, which can be expected because of the much smaller excess energies for the $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ formation compared with $O_2(^3\Sigma_g^-)$ formation, would draw the deactivation in the pCT channel more to the singlet side than it would be the case, if isc would not compete with ic. However, the deviation from unity is not very large and could also be the consequence of experimental uncertainties caused by the only small CT effects.

It is striking that for the BPs, most values of $k_{CT}^{1\Delta}$ are larger than $k_{CT}^{1\Sigma}$ despite the smaller energy gap for the formation of $O_2(^1\Sigma_g^+)$ (see also Figure 3). The opposite was found for the NDs and the BDs, for which the values of $k_{CT}^{1\Sigma}$ are on an average 2-fold larger than the $k_{CT}^{1\Delta}$ values in accordance with the energy gap relation. The violation of this relation by the $T_1(n\pi^*)$ ketones lends support to our earlier speculation that the concomitant one-center orbital jump of the electron in the $n\pi^* \rightarrow n^2$ transition at the ketone O atom couples to the simultaneous change of the orbital angular momentum accompanying the $^3\Sigma \rightarrow {}^1\Delta$ transition of O_2, thus enhancing the $^1(T_1(n\pi^*)\cdot{}^3\Sigma) \rightarrow {}^1(S_0(n^2)\cdot{}^1\Delta)$ transition.[24] Actually, such a coupling effect is impossible in the $^1(T_1(n\pi^*)\cdot{}^3\Sigma) \rightarrow {}^1(S_0(n^2)\cdot{}^1\Sigma)$ transition, since there is no change of orbital angular momentum of O_2 in the accompanying the $^3\Sigma \rightarrow {}^1\Sigma$ transition.

However, most of the strong deviation of overall rate constants $k_T^{1\Delta}$ of $T_1(n\pi^*)$ sensitizers to larger values than expected from the excess energy dependence $f(\Delta E)$ of the rate constants of ic of $(T_1(\pi\pi^*)\cdot{}^3\Sigma)$ nCT complexes cannot be explained by the speculation of orbital angular momentum coupling, as we assumed earlier.[24] We now realize that due to the concomitant large structural changes a different function $f(\Delta E)$ describes the excess energy dependence of the rate constants of ic of $(T_1(n\pi^*)\cdot{}^3\Sigma)$ nCT complexes leading to much larger rate constants for the ic of $(T_1(n\pi^*)\cdot{}^3\Sigma)$ complexes in the high excess energy region because the much weaker dependence on ΔE. Thus, changes in the electronic configuration of T_1 leading to corresponding structural changes are the principal reason for the different behavior of $T_1(n\pi^*)$ and $T_1(n\pi^*)$ singlet oxygen sensitizers.

Conclusions

The comparative analysis of the rate constants of formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ in the quenching of $n\pi^*$ and $\pi\pi^*$ triplet states by O_2 reveals common behavior and important differences. The quenching proceeds for both $T_1(n\pi^*)$ and $T_1(\pi\pi^*)$ sensitizers 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 channel originates from excited $^{1,3}(T_1\cdot{}^3\Sigma)$ complexes with no particular CT character and the other channel from $^{1,3}(T_1\cdot{}^3\Sigma)$ exciplexes with partial CT character. Energy gap relations determine via the respective ΔE 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. In the pCT channel, the rate constants vary on a logarithmic scale apparently linearly with ΔG_{CET}. However, both the ΔE dependence of the nCT rate constants and the ΔG_{CET} dependence of the pCT rate constants are much weaker for the $T_1(n\pi^*)$ sensitizers.

The comparison with the CT induced quenching of $O_2(^1\Delta_g)$ by ground-state BP and BD sensitizers reveals that the different electronic configuration $n\pi^*$ versus $\pi\pi^*$ leads to different sterical structures of $^{1,3}(T_1\cdot{}^3\Sigma)$ complexes: a reduced four-center structure of $^{1,3}(T_1(n\pi^*)\cdot{}^3\Sigma)$ complexes and an extended supra-supra structure of $^{1,3}(T_1(\pi\pi^*)\cdot{}^3\Sigma)$ complexes. These differences strongly influence the complex deactivation, which is accompanied by large structural changes only for $^{1,3}(T_1(n\pi^*)\cdot{}^3\Sigma)$ complexes. Consequently, a weaker ΔE dependence of $\log(F'(\Delta E))$ results for the ic of $^{1,3}(T_1(n\pi^*)\cdot{}^3\Sigma)$ complexes. The much weaker CT effects found with $T_1(n\pi^*)$ BPs are also the result of the different structures of $^{1,3}(T_1\cdot{}^3\Sigma)$ complexes. The influence of electron donating or electron withdrawing substituents is only large if they are directly bound to the reaction center, which is not the case for the four-center structure of the $^{1,3}(T_1(n\pi^*)\cdot{}^3\Sigma)$ pCT complexes.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Adolf Messer Stiftung is gratefully acknowledged. C. S. thanks the Ministère de la Culture, de l'Enseignement Supérieur et de la Recherche of Luxembourg, for the award of a BFR scholarship.

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) Schmidt, R.; Bodesheim, M. *J. Phys. Chem. A* **1998**, *102*, 4769.

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

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

(11) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 708.

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

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

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

(15) Grewer, C.; Brauer, H.-D. *J. Phys. Chem.* **1994**, *98*, 4230.

(16) Grewer, C.; Wirp, C.; Neumann, M.; Brauer, H.-D. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 997.

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

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

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

(20) Abdel-Shafi, A. A.; Wilkinson, F. *J. Phys. Chem. A* **2000**, *104*, 5747.

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

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

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

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

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

(26) Schmidt, R.; Shafii, F.; Schweitzer, C.; Abdel-Shafi, A. A.; Wilkinson, F. *J. Phys. Chem. A* **2001**, *105*, 1811.

(27) Schmidt, R.; Shafii, R. *J. Phys. Chem. A* **2001**, *105*, 8871.

(28) Netto-Ferreira, J. C.; Scaiano, J. C. *Photochem. Photobiol.* **1991**, *54*, 17.

(29) Bendig, J.; Schmidt, R.; Brauer, H.-D. *Chem. Phys. Lett.* **1993**, *202*, 535.

(30) Nau, W. M.; Scaiano, J. C. *J. Phys. Chem.* **1996**, *100*, 11360.

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

(32) Gorman, A. A.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1986**, *108*, 5074.

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

(34) Darmanyan, A. P.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 3723.

(35) Darmanyan, A. P.; Foote, C. S. *J. Phys. Chem.* **1993**, *97*, 4573.

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

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

(38) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

(39) El-Sayed, M. A. *J. Chem. Phys.* **1964**, *41*, 2462.

(40) Porter, G.; Suppan, P. *Trans. Faraday Soc.* **1965**, *61*, 1664.

(41) Schweitzer, C.; Mehrdad, Z.; Noll, A.; Grabner, E.-W.; Schmidt, R. *Helv. Chim. Acta* **2001**, *84*, 2493.

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

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

(44) The viscosities of cyclohexane and TET amount to 0.975 and 0.969 mPas at 20 °C, ref 42. Therefore we take the value $k_{\mathrm{diff}} = 2.72 \times 10^{10}$ M^{-1}s^{-1} derived in ref 19 for cyclohexane to be also valid for TET.

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

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

(47) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983.

(48) Weller, A. *Z. Phys. Chem. Neue Folge* **1982**, *133*, 93.

(49) Kadish, K. M.; Morrison, M. M. *J. Am. Chem. Soc.* **1976**, *98*, 3326.

(50) Leung, H.-K.; Wu, G.-Z.; Gan, W.-X.; Chan, Y.-Y. *J. Chem. Soc., Chem. Commun.* **1987**, 20.

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

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

(53) The empirical curve is $f(\Delta E) = 9.05 + 9 \times 10^{-3}\Delta E - 1.15 \times 10^{-4}\Delta E^2 + 1.15 \times 10^{-7}\Delta E^3 + 9.1 \times 10^{-11}\Delta E^4$.

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

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

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

(57) Schweitzer, C.; Mehrdad, Z.; Shafii, F.; Schmidt, R. *J. Phys. Chem. A* **2001**, *105*, 5309.

(58) Schweitzer, C.; Mehrdad, Z.; Shafii, F.; Schmidt, R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3095.

(59) Aubry, J. M.; Mandard-Cazin, B.; Rougee, M.; Bensasson, R. V. *J. Am. Chem. Soc.* **1995**, *117*, 9159.

(60) Bobrowski, M.; Liwo, A.; Oldziej, S.; Jeziorek D.; Ossowski, T. *J. Am. Chem. Soc.* **2000**, *122*, 8112.

(61) Herzberg, G. *Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950; p 560.

(62) Kamei, S.; Sato, T.; Mikami, N.; Ito, M. *J. Phys. Chem.* **1986**, *90*, 5615.

(63) $k_{\mathrm{T}}^{\mathrm{Q}} = 1.0 \times 10^{10}$ M^{-1} s^{-1} and $S_{\Delta} = 0.26$ have recently been determined for AMBP in TET ($E_{\mathrm{T}} = 282$ kJ mol^{-1}, $E_{\mathrm{ox}} = 1.26$ vs Ag/AgCl),[41] from which $\log(k_{\mathrm{CT}}^{3\Sigma}/3) = 9.582$ is calculated. *a* could not be quantified, due to the weak O$_2$($^1\Sigma_g^+$) emission preventing the determination of $\log(k_{\mathrm{CT}}^{1\Sigma})$ and $\log(k_{\mathrm{CT}}^{1\Delta})$.