Oxygen Quenching of nπ* Triplet Phenyl Ketones: Local Excitation and Local Deactivation

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Dedicated to Professor *André M. Braun* on the occasion of his 60th birthday

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We have studied the charge-transfer-induced deactivation of nπ* excited triplet states of benzophenone derivatives by $O_2(^3\Sigma_g^-)$, and the charge-transfer-induced deactivation of $O_2(^1\Delta_g)$ by ground-state benzophenone derivatives in CH_2Cl_2 and CCl_4. The rate constants for both processes are described by *Marcus* electron-transfer theory, and are compared with the respective data for a series of biphenyl and naphthalene derivatives, the triplet states of which have $\pi\pi$* configuration. The results demonstrate that deactivation of the locally excited nπ* triplets occurs by local charge-transfer and non-charge-transfer interactions of the oxygen molecule with the ketone carbonyl group. Relatively large intramolecular reorganization energies show that this quenching process involves large geometry changes in the benzophenone molecule, which are related to favorable *Franck-Condon* factors for the deactivation of ketone-oxygen complexes to the ground-state molecules. This leads to large rate constants in the triplet channel, which are responsible for the low efficiencies of $O_2(^1\Delta_g)$ formation observed with nπ* excited ketones. Compared with the deactivation of $\pi\pi$* triplets, the non-charge-transfer process is largely enhanced, and charge-transfer interactions are less important. The deactivation of singlet oxygen by ground-state benzophenone derivatives proceeds *via* interactions of $O_2(^1\Delta_g)$ with the Ph rings.

Introduction. – In the presence of molecular oxygen, the main pathway of deactivation of excited triplet states of sufficient energy E_T is quenching by $O_2(^3\Sigma_g^-)$, which leads to formation of the excited singlet states $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$, and the ground-state $O_2(^3\Sigma_g)$, with efficiencies depending on several parameters [1–9][16–19][20]. The influence of the electronic configuration of a sensitizer on the efficiency S_Δ of $O_2(^1\Delta_g)$ generation has been one of the most puzzling issues in singlet-oxygen photochemistry [1–9]. Although exceptions are known [8][9], S_Δ values are generally found to be significantly lower with nπ* triplet states ($S_\Delta \approx 0.3-0.5$) than with $\pi\pi$* triplet states ($S_\Delta \approx 0.8-1.0$) [1–7]. Several features of the investigated nπ* triplets have been evoked to explain this behavior, such as their high polarizability [3], high triplet energies [7], or large *Franck-Condon* factors for the deactivation of ketone-oxygen complexes [4], but no clear mechanistic proof has been given. The aim of the present work is to determine the structure of the charge-transfer (CT) complexes formed with molecular oxygen and aromatic ketones having nπ* triplet-state configuration. Excited CT complexes play an important role in the deactivation of triplet-excited ketones by ground-state oxygen, and in the quenching of excited singlet oxygen by the ground-state ketones. These two processes will be compared with each other, and with the respective processes with naphthalene and biphenyl derivatives, the T_1-states of which have $\pi\pi$* configuration. Significant information on the nature of the

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intermediate CT structures formed with the latter compounds is available from chemical reactions of $O_2(^1\Delta_g)$ with 1,4-substituted naphthalene derivatives [10], from *ab initio* calculations [11], and from previous comparative investigations [12][13]. A series of benzophenone derivatives was chosen in our study for several reasons: *i*) the T_1-state configuration of *para*-halogen-, *para*-MeO, and nonsubstituted benzophenone derivatives is undoubtedly $n\pi^*$ in polar and nonpolar solvents [14], and also *triplet para*-aminobenzophenone is at least partially $n\pi^*$ in nonpolar solvents [14][15]; *ii*) previously observed correlations of the rate constants for oxygen-quenching of the T_1 states of benzophenone derivatives with *Hammett* σ^+ values demonstrate that exciplex formation does actually occur during this process [1]; *iii*) substitution induces large changes in the oxidation potential E_{ox} of benzophenone, but has very little effect on its triplet energy E_T; *iv*) benzophenone differs from biphenyl only by the central C=O group, and hence a comparison with this compound will be most informative.

Results. – The rate constants k_T^Q of T_1 state quenching by O_2 and the corresponding overall efficiencies S_Δ of $O_2(^1\Delta_g)$ sensitization in CH_2Cl_2 (DCM) and CCl_4 (TET) of the differently substituted benzophenone derivatives are listed in *Table 1* together with their triplet state energies.

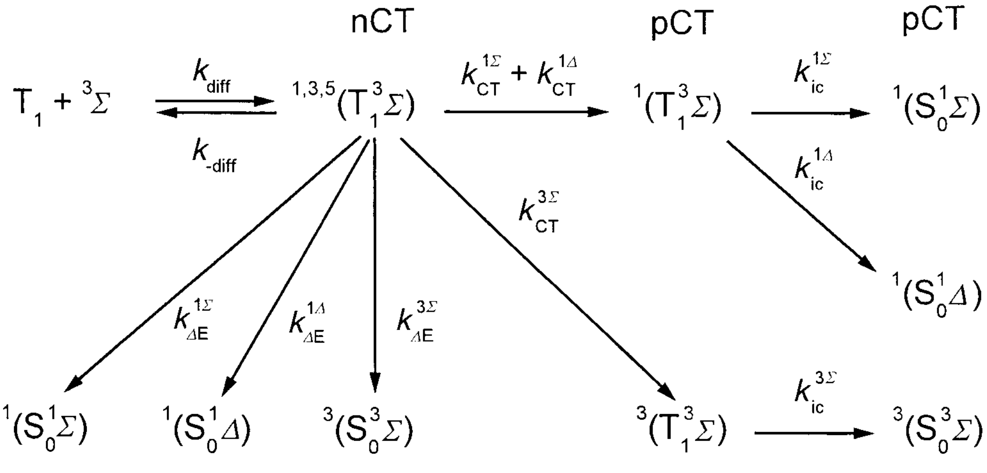
Table 1. *Rate Constants* k_T^Q *and Singlet-Oxygen-Formation Efficiencies* S_Δ, *for Oxygen Quenching of the* T_1 *States of Benzophenone Derivatives in DCM and TET, and Their Triplet Energies* E_T.

		DCM		TET	
Substituent	E_T/kJ mol^{-1} a)	S_Δ d)	$k_T^Q/10^9 M^{-1} s^{-1}$ e)	S_Δ d)	$k_T^Q/10^9 M^{-1} s^{-1}$ e)
4-NH_2	282			0.26 f)	10.0
4,4′-Dimethoxy	293	0.35	9.80	0.36	3.88
4-MeO	290	0.35	6.35	0.39	3.10
3,4′-Dimethyl	287 b)	0.38	2.60	0.43	1.88
4-Me	289 c)	0.38	3.25	0.44	1.90
None	287	0.40	1.84	0.45	1.80
4-Br	289 c)	0.37	2.34	0.49	1.30
4-Cl	287 c)	0.36	2.04	0.46	1.40
4,4′-Dichloro	286 c)	0.42	1.71	0.48	1.07
4-CN	279 c)	0.50	1.26	0.53	0.622

a) ± 4 kJ mol^{-1}. b) From [21]. c) From [7]. d) ± 4%. e) ± 10%. f) In O_2-saturated TET.

Scheme 1 is used to discuss the kinetics of the deactivation of T_1 states by $O_2(^3\Sigma_g^-)$ $(= {^3\Sigma})$. Encounter complexes with singlet, triplet, and quintet multiplicity with no particular CT character (nCT) are formed. $^{1,3}(T_1{^3\Sigma})$ nCT complexes decay by internal conversion (ic), with rate constants $k_{\Delta E}^{1\Sigma}$ $k_{\Delta E}^{1\Delta}$, and $k_{\Delta E}^{3\Sigma}$, to nCT complexes $^1(S_0{^1\Sigma})$, $^1(S_0{^1\Delta})$, and $^3(S_0{^3\Sigma})$, which finally dissociate to yield ground-state sensitizer S_0 and $O_2(^1\Sigma_g^+)$ $(= {^1\Sigma})$, $O_2(^1\Delta_g)$ $(= {^1\Delta})$, and $O_2(^3\Sigma_g^-)$, respectively [6][16]. ic competes with the formation of exciplexes with partial CT character (pCT), *i.e.*, $^1(T_1{^3\Sigma})$ with rate constant $(k_{CT}^{1\Sigma} + k_{CT}^{1\Delta})$, or $^3(T_1{^3\Sigma})$ with rate constant $k_{CT}^{3\Sigma}$. ic of these exciplexes, (with rate constants $k_{ic}^{1\Sigma}$, $k_{ic}^{1\Delta}$, and $k_{ic}^{3\Sigma}$) leads, *via* pCT complexes $^1(S_0{^1\Sigma})$, $^1(S_0{^1\Delta})$, and $^3(S_0{^3\Sigma})$, to the CT-induced formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$, respectively [16]. It has been demonstrated that formation of pCT complexes is the rate-determining step

Scheme 1



during oxygen quenching of triplet-excited naphthalene and biphenyl derivatives [16]. We will assume that exciplex formation is also rate-determining in the deactivation of benzophenone derivatives.

No direct product channel exists for the quintet nCT complex, but ${}^5(T_1{}^3\Sigma)$ nCT might contribute to the singlet- and triplet-deactivation channels by isc to ${}^{1,3}(T_1{}^3\Sigma)$ nCT, as demonstrated by the observation of T_1 deactivation rate constants k_T^Q significantly exceeding the spin-statistical limit of four ninth of the diffusion-controlled rate constant k_{diff} for the singlet and triplet channels with several sensitizers [17]. Therefore, we evaluate the overall rate constant $k_{D,T}$ of the deactivation of nCT complexes ${}^{1,3,5}(T_1{}^3\Sigma)$ by *Eqn. 1*, assuming that these complexes are formed with rate constant k_{diff} and either dissociate back to T_1 and $O_2({}^3\Sigma_g^-)$ with rate constant k_{-diff} or deactivate with rate constant $k_{D,T}$ to the products ground-state sensitizer S_0 and $O_2({}^1\Sigma_g^+)$, $O_2({}^1\Delta_g)$, or $O_2({}^3\Sigma_g^-)$.

$$k_{D,T} = k_{-diff}k_T^Q/(k_{diff} - k_T^Q) \tag{1}$$

The overall rate constant of formation of $O_2({}^3\Sigma_g^-)$ is given as $(1 - S_\Delta)k_{D,T}$, where S_Δ is the efficiency of formation of $O_2({}^1\Delta_g)$. The rate constant $k_{CT}^{3\Sigma}$ of formation of $O_2({}^3\Sigma_g^-)$ *via* the triplet pCT channel is obtained by subtracting the contribution of the nCT deactivation pathway from the overall rate constant of formation of $O_2({}^3\Sigma_g^-)$:

$$k_{CT}^{3\Sigma} = k_{D,T}(1 - S_\Delta) - k_{\Delta E}^{3\Sigma} \tag{2}$$

To evaluate the contribution of the nCT pathway, we shall consider that the rate constants $k_{\Delta E}^{1\Sigma}$, $k_{\Delta E}^{1\Delta}$, and $k_{\Delta E}^{3\Sigma}$ of formation of $O_2({}^1\Sigma_g^+)$, $O_2({}^1\Delta_g)$, and $O_2({}^3\Sigma_g^-)$ in the nCT channel are expected to be proportional to the rate constants of the respective ic processes, which depend, *via Eqn. 3* [18],

$$k_{ic} = (4\pi^2/h)\rho(\Delta E)F(\Delta E)\beta^2 \tag{3}$$

on the electronic coupling matrix element β, the *Franck-Condon* factors $F(\Delta E)$, the density of final states $\rho(\Delta E)$, and, hence, on the excess energy ΔE. We have recently described a common ΔE dependence of the multiplicity-normalized rate constants of formation $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ during O_2 quenching of a series of nCT triplet sensitizers in TET [16]. On the basis of this empirical relationship with the average value of $\Delta E = E_T = 287$ kJ mol^{-1} for this series of benzophenone derivatives, $k_{\Delta E}^{3\Sigma}$ is calculated to be 9.4×10^5 s^{-1}. However, this empirical curve was obtained with $\pi\pi^*$ triplets only, and deviations were observed with $n\pi^*$ excited sensitizers. Nonetheless, we will assume that the nCT contribution is negligible in the present case, since the calculated value is more than by two orders of magnitude smaller than the smallest experimental rate constant of formation of $O_2(^3\Sigma_g^-)$ obtained in this study (see *Table 1*). Hence, the rate constant of CT-induced formation of $O_2(^3\Sigma_g^-)$ is calculated by $k_{CT}^{3\Sigma} = k_{D,T}\,(1 - S_\Delta)$.

Scheme 2 is used to discuss the kinetics of the deactivation of $O_2(^1\Delta_g)$ by ground-state benzophenone derivatives. One singlet nCT encounter complex $^1(S_0{}^1\Delta)$ is formed with a spin-statistical weight of unity, and deactivated either by collisional electronic to vibrational energy transfer to the terminal bonds of the quencher (with rate constant k_{ev}), or by formation of a pCT exciplex, and subsequent intersystem crossing (rate constant k_{isc}), leading to the ground states. Our results suggest that exciplex formation is the rate-determining step in the CT-induced deactivation of $O_2(^1\Delta_g)$ [12][13]. The rate constant for this process is thus given by *Eqn. 4*,

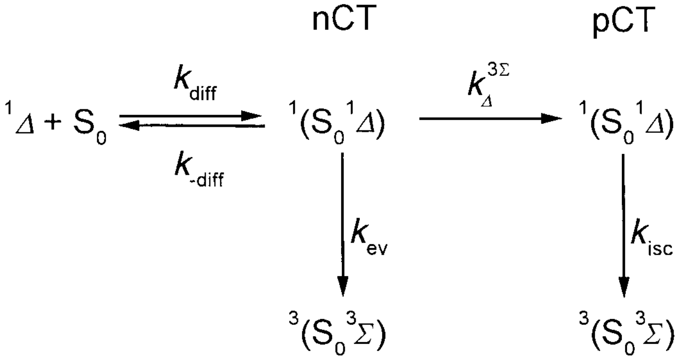
$$k_\Delta^{3\Sigma} = k_{D,\Delta} - k_{ev} \tag{4}$$

where $k_{D,\Delta} = k_{-diff}k_\Delta^Q/(k_{diff} - k_\Delta^Q)$, and k_Δ^Q is the experimental rate constant of $O_2(^1\Delta_g)$-quenching by the benzophenone derivative. We assume for both quenching processes $k_{-diff} = gk_{diff}/\mathrm{M}^{-1}$, with $g = 1$, whereby $\mathrm{M} = \mathrm{mol\ l}^{-1}$, as was already done by *Wilkinson* and *Abdel-Shafi* [19], and ourselves [12][13][16]. A larger value of g would lead to proportionally larger values for all nCT complex deactivation rate constants, but the relative changes of $k_{D,T}$ and $\mathrm{k}_{D,\Delta}$ would remain the same.

The rate constant k_{ev} of e-v deactivation is obtained for each derivative by *Eqn. 5*,

$$k_{ev} = \Sigma N_{XY} k_{XY} \tag{5}$$

Scheme 2



where N_{XY} is the number of terminal X–Y bonds per quencher molecule. The rate constants k_{XY} of e-v deactivation by one terminal bond have been determined to be $k_{(NH)} = 1530\ \text{M}^{-1}\text{s}^{-1}$ [10], $k_{(CH)\text{aromatic}} = 494\ \text{M}^{-1}\text{s}^{-1}$ [22] and $k_{(CH)\text{aliphatic}} = 309\ \text{M}^{-1}\text{s}^{-1}$ [22]. The e-v deactivation by other terminal bonds is negligible because of their significantly lower vibrational frequencies [22]. *Table 2* lists the rate constants k_{ev} and k_{Δ}^{Q} determined in DCM for four substituted benzophenone derivatives, as well as their oxidation potentials.

Table 2. *Experimental* (k_{Δ}^{Q}) *and e-v* (k_{ev}) *Rate Constants of Singlet-Oxygen Quenching by Benzophenone Derivatives in DCM, and Their Oxidation Potentials* E_{ox}

Quencher	E_{ox}/V *vs.* SCE [a])	$k_{\Delta}^{Q}/10^4\text{M}^{-1}\ \text{s}^{-1}$ [b])	$k_{ev}/10^4\text{M}^{-1}\ \text{s}^{-1}$
Michler's ketone	0.86	2410	0.77
4-(Dimethylamino)benzophenone	1.06	496	0.63
2-Aminobenzophenone	1.18	210	0.75
2,4,6-Trimethoxybenzophenone	1.65	4.56	0.62

[a]) Calculated from the values measured *vs.* Ag/AgCl, by subtracting 0.09 V. Error: ± 0.02 V. [b]) ± 7%.

All other oxidation potentials measured *vs.* Ag/AgCl reference electrode are listed in *Table 3*. No oxidation peaks were observed with the halogenated ketones. 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 [23]. 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 benzophenone derivatives and a series of biphenyl derivatives, for which reliable oxidation potentials have been determined *vs.* SCE = Ag/AgCl – 0.09 V [20]. The conversion constant of 0.09 V was obtained by measuring the oxidation potentials of several biphenyl derivatives and other reference compounds *vs.* Ag/AgCl reference electrode. The data of *Table 3* yield the relationship

Table 3. *Oxidation Potentials* (E_{ox}) *of Biphenyl and Benzophenone Derivatives*

Substituent	Biphenyl	Benzophenone	
	E_{ox}/V *vs.* SCE [a])	E_{ox}/V *vs.* Ag/AgCl [b])	E_{ox}/V *vs.* SCE [c])
4-NH_2		1.26	
4,4′-Dimethoxy	1.30	2.20	2.00
4-MeO	1.53	2.20	2.25
3,4-Dimethyl		2.45	2.42
4,4′-Dimethyl	1.69		
4-Me	1.80	2.60	2.53
None	1.91	2.85	2.65
4-Br	1.95		2.69
4-Cl	1.96		2.71
4,4′-Dichloro	2.02		2.77
4-CN	2.11		2.87

[a]) From [20]. [b]) Measured values. [c]) Estimated by the correlation E_{ox}(benzophenones) = 0.61 + 1.07 E_{ox}(biphenyls).

E_{ox}(benzophenones) $= 0.61 + 1.07$ E_{ox}(biphenyls), which is used to estimate the oxidation potentials of the benzophenone derivatives.

We will compare two CT-induced processes leading, *via* intermediates of different statistical weight, to the quenching of T_1 and $O_2(^1\Delta_g)$. Since the overall rate constants of triplet-state quenching of benzophenone derivatives by O_2 are much smaller than the spin-statistical limit of $4/9k_{diff}$ (see *Table 1*), it is unlikely that the $^5(T_1{}^3\Sigma)$ quintet complex significantly contributes to its formation in this case. Therefore, we account for the threefold smaller statistical weight of the intermediate $^3(T_1{}^3\Sigma)$ nCT complex compared with the $^1(S_0{}^1\Delta)$ nCT complex by multiplying $k_{CT}^{3\Sigma}$ with the factor 3. As a general designation for the rate constant of CT induced quenching, we will use k_{CT} for both $3k_{CT}^{3\Sigma}$ and $k_{\Delta}^{3\Sigma}$. k_{CT} is related to the activation free energy $\Delta G^{\#}$ of pCT complex formation by *Eqn. 6*,

$$\Delta G^{\#} = -RT \ln\left(\frac{k_{CT}}{k_B T/h}\right) \tag{6}$$

where k_B and h are the *Boltzmann* and *Planck* constants, respectively, and T is the temperature in K. Both $\Delta G^{\#}$ and k_{CT} can be correlated with the free-energy change ΔG_{CET} for a complete electron transfer from the sensitizer to O_2, which is obtained by *Eqn. 7*, according to *Weller* [24]:

$$\Delta G_{CET} = F(E_{ox} - E_{red}) - E_{exc} + \frac{e^2}{2}\left(\frac{1}{r^+} + \frac{1}{r^-}\right)\left(\frac{1}{\varepsilon_S} - \frac{1}{37}\right) - \frac{e^2}{\varepsilon_S(r^+ + r^-)} \tag{7}$$

F is the *Faraday* constant, e is the elementary charge ($e^2 = 14.43$ eV Å). E_{ox} is the oxidation potential of the donor measured in MeCN (ACN), E_{red} the reduction potential of molecular oxygen (-0.78 V *vs.* SCE in ACN [25]), E_{exc} is the excitation energy, *i.e.*, the state energy E_T of the quenched sensitizer triplet, or the state energy $E_\Delta = 94$ kJ mol^{-1} of the quenched $O_2(^1\Delta_g)$. The static dielectric constant ε_s of the solvent is 2.238 in TET and 9.08 in DCM [21]. The radius r^+ of the electron donor does not vary significantly within a series of benzophenone derivatives; hence, we will use the representative mean value of 3.62 Å, from 3.45 Å for benzophenone and 3.78 Å for dimethoxybenzophenone, to account for the whole series. r^- of the acceptor O_2 is 1.73 Å. Molecular radii have been obtained from the *Van der Waals* volumes estimated according to *Bondi* [26], assuming a spherical molecular shape. With these values, we calculate the size-dependent electrostatic interaction energy of *Eqn. 7* to be 133.5 kJ mol^{-1} in TET and 20.8 kJ mol^{-1} in DCM. *Tables 4–6* list the driving-force-dependent rate constants k_{CT} for quenching by O_2 of T_1-excited benzophenones and quenching by ground-state benzophenones of $O_2(^1\Delta_g)$, as well as the driving forces ΔG_{CET}. The corresponding data for a series of biphenyl [13] and naphthalene [12] derivatives is given for comparison.

Discussion. – *Fig. 1* shows the dependence of $\log(k_{CT})$ on the free-energy change ΔG_{CET}, for both CT-induced quenching of excited triplet sensitizers by ground-state oxygen, and CT-induced quenching of $O_2(^1\Delta_g)$ by the ground-state sensitizers (data from *Tables 4* and *6*). We have previously noted that, in the case of biphenyl derivatives (open symbols in *Fig. 1* [13]) and naphthalene derivatives ([12], not shown), the rate

Table 4. *Driving Forces* (ΔG_{CET}) *and Rate Constants* (k_{CT}) *for the CT-Induced Deactivation of Triplet-Excited Benzophenone and Biphenyl Derivatives by* $O_2(^3\Sigma_g^-)$*, in DCM and TET*

Substituent	Benzophenone/DCM		Benzophenone/TET		Biphenyl/DCM [a])		Biphenyl/TET [a])	
	ΔG_{CET}/ kJ mol^{-1}	k_{CT}/ $10^9\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	ΔG_{CET}/ kJ mol^{-1}	k_{CT}/ $10^9\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	ΔG_{CET}/ kJ mol^{-1}	k_{CT}/ $10^9\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	ΔG_{CET}/ kJ mol^{-1}	k_{CT}/ $10^9\mathrm{M}^{-1}\,\mathrm{s}^{-1}$
4-NH_2			39.6	35.11				
4,4′-Dimethoxy	– 4.0	24.98	108.7	8.69	– 44.7	60.00	68.3	57.09
4-MeO	23.1	14.63	135.8	6.40	– 26.5	27.16	86.5	9.04
3,4-Dimethyl	42.5	5.16	155.2	3.45				
4,4′-Dimethyl					– 10.1	8.25	102.9	2.65
4-Me	51.6	6.54	164.3	3.43	– 2.5	7.49	110.5	1.25
None	64.7	3.45	177.4	3.18	6.1	3.85	119.1	0.85
4-Br	66.6	4.68	179.3	2.09	18.0	4.50	131.0	0.31
4-Cl	70.5	4.24	183.2	2.39	16.0	3.31	129.0	0.40
4,4′-Dibromo					24.8	1.70	137.8	0.12
4,4′-Dichloro	77.3	3.09	190.0	1.74	25.7	1.28	138.7	0.24
4-CN	96.0	1.94	208.7	0.90			147.4	0.12

[a]) From [13].

Table 5. *Driving Forces* (ΔG_{CET}) *and Rate Constants* (k_{CT}) *for the CT-Induced Deactivation of Triplet-Excited Naphthalene Derivatives by* $O_2(^3\Sigma_g^-)$*, in TET.* Data from [12].

Sensitizer	ΔG_{CET}/kJ mol^{-1}	k_{CT}/$10^9\mathrm{M}^{-1}\,\mathrm{s}^{-1}$
1-Methoxynaphthalene	74.8	6.31
Acenaphthene	88.5	3.90
2-Methoxynaphthalene	89.4	1.92
2,6-Dimethylnaphthalene	101.0	1.35
1-Methylnaphthalene	100.8	1.04
2-Methylnaphthalene	111.6	0.81
Naphthalene	113.4	0.50
1-Bromonaphthalene	133.0	0.059
Naphthalene-1-carbonitrile	160.2	0.060

Table 6. *Driving Forces* (ΔG_{CET}) *and Rate Constants* (k_{CT}) *for the CT-Induced Deactivation of* $O_2(^1\Delta_g)$ *by Benzophenone and Biphenyl Derivatives in DCM*

Quencher	ΔG_{CET}/kJ mol^{-1}	k_{CT}/$10^4\mathrm{M}^{-1}\,\mathrm{s}^{-1}$
Michler's ketone	85.0	2409
4-Dimethylaminobenzophenone	104.3	495
2-Aminobenzophenone	115.9	209
2,4,6-Trimethoxybenzophenone	161.2	3.93
4,4′-Dimethoxybiphenyl [a])	127.3	16.85
4-Methoxybiphenyl [a])	149.5	3.92
4,4′-Dimethylbiphenyl [a])	164.9	0.380
4-Methylbiphenyl [a])	175.5	0.401

[a]) From [13].

constants for both CT-induced deactivation processes are described by one common dependence on ΔG_{CET}. The solid line in *Fig. 1* is a fit to the data of the biphenyl derivatives, according to the *Marcus* equation,

$$\varDelta G^{\#} = \frac{\lambda}{4}\left(1 + \frac{\delta^2 \Delta G_{\mathrm{CET}}}{\lambda}\right)^2 \tag{8}$$

which describes the activation free energy $\varDelta G^{\#}$ of a charge-transfer step, as a function of the reorganization energy λ, and the driving force $\delta^2 \varDelta G_{\mathrm{CET}}$ [27]. δ is a fit parameter, which has been introduced to correct $\varDelta G_{\mathrm{CET}}$ for the partial CT nature of these processes [12][13]. The validity of one single pair of λ and δ values for both deactivation processes, which is a consequence of the common dependence of $\log(k_{\mathrm{CT}})$ or $\varDelta G^{\#}$ on $\varDelta G_{\mathrm{CET}}$, has been explained by the involvement of a common charge-transfer intermediate in these two processes. This was also supported by the equivalence of the dipole moments of the transition states towards pCT-complex formation in both processes [12]. The kinetic behavior observed with the naphthalene derivatives is almost identical to that of the biphenyls (see *Fig. 2*), they differ only by a slight shift to lower k_{CT} values for the naphthalenes, which has been explained by a larger electronic delocalization, leading to larger reorganization energies [13]. Hence, it is strongly suggested that a driving-force dependence of $\log(k_{\mathrm{CT}})$ as described by the solid line in *Fig. 1*, is indicative of the formation of an exciplex with molecular oxygen and a phenyl ring. Such a complex has been described in a recent MCSCF study of the deactivation of $O_2(^1\varDelta_g)$ by benzene as a supra-supra CT transition structure, where the O_2 molecule is bound to the C_6H_6 ring in 1,4-position [11]. The two processes leading to its formation in the case of biphenyl are represented in *Scheme 3*.

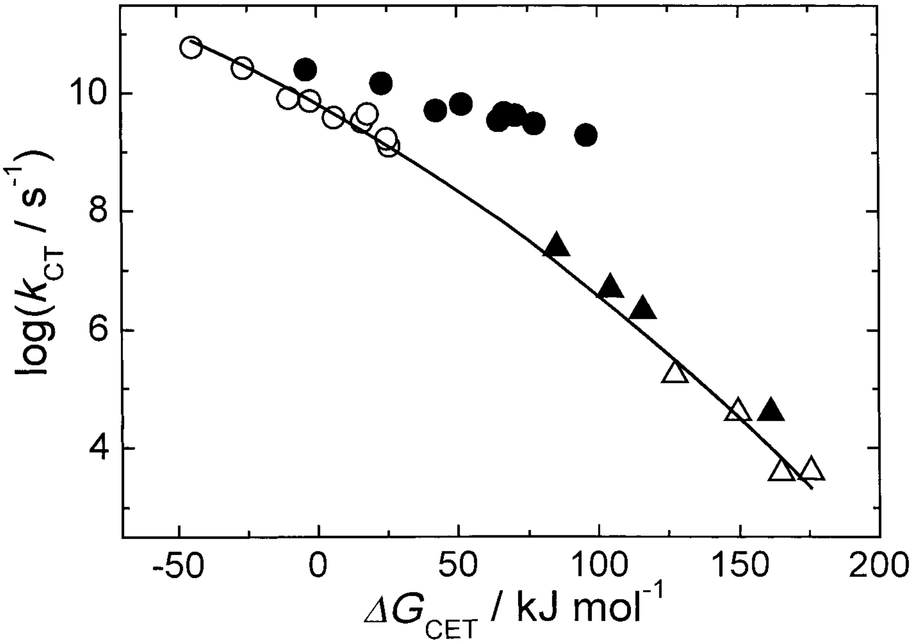
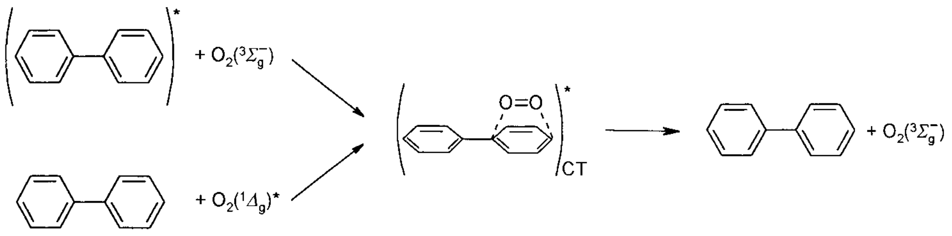


Fig. 1. *Driving-force dependence of the rate constants of CT-induced deactivation of* T_1 *by* $O_2(^3\Sigma_g^-)$ (circles), *and of CT-induced deactivation of* $O_2(^1\varDelta_g)$ *by* S_0 (triangles), *for a series of benzophenone derivatives* (solid symbols) *and biphenyl derivatives* (open symbols) *in DCM.* For details, see text.

Scheme 3



Let us now consider the data obtained with the benzophenone derivatives in this context. Clearly, the rate constants for the CT-induced deactivation of $O_2(^1\Delta_g)$ by the benzophenones depend in a very similar way on ΔG_{CET}, and it seems that this process also occurs *via* formation of an exciplex of the excited oxygen molecule with one phenyl moiety. In contrast, the rate constants for the deactivation of the benzophenones triplet states differ significantly from the correlation: the lowest experimental values exceed the fit values by almost three orders of magnitude, which is far beyond experimental uncertainties, and indicates, for the first time, that exciplex formation during oxygen quenching of nπ* excited benzophenone triplet states occurs by a mechanism *not* involving a binding of the O_2 molecule to a phenyl ring. It is very important to note in this respect that the kinetic behavior of the deactivation of $O_2(^1\Delta_g)$ by benzophenone derivatives is equivalent to that of its deactivation by biphenyl derivatives. This ensures that the deviations observed with the T_1-state quenching process are not a consequence of any specific structural effects due to the conformation of the benzophenone molecule.

We may now focus on the deactivation of triplet states by $O_2(^3\Sigma_g^-)$. *Fig. 2* shows the dependence of $\log(k_{CT})$ on ΔG_{CET}, for a series of benzophenone, biphenyl, and naphthalene derivatives, in TET. The differences in the kinetic behavior become even more striking than before. For both $\pi\pi$* excited naphthalene and biphenyl derivatives, we observe a rather sharp dependence of $\log(k_{CT})$ on ΔG_{CET} (an increase of the rate constant by three orders of magnitude corresponds to a change in E_{ox} from 2.11 to 1.14 V *vs.* SCE), whereas the driving-force dependence is much weaker with the nπ* excited benzophenone derivatives (the rate constant increases by less than two orders of magnitude, while E_{ox} changes from 2.87 to 1.17 V *vs.* SCE).

This means that charge-transfer interactions are significantly weaker in the complexes formed with the nπ* excited triplets. Moreover, since the rate constants of formation of $O_2(^3\Sigma_g^-)$ are markedly larger in the high-ΔG_{CET} region, we need to conclude that the $^3(T_1(n\pi^*)^3\Sigma) \rightarrow {}^3(S_0(n^2)^3\Sigma)$ transition is specifically enhanced by a non CT-dependent contribution. This is, in spite of the larger triplet energies (E_T(benzophenones) ≈ 287 kJ mol^{-1} *vs.* E_T(biphenyls) ≈ 268 kJ mol^{-1} [20], and E_T(naphthalenes) ≈ 250 kJ mol^{-1} [12]), which should lead to lower values of $k_{\Delta E}^{3\Sigma}$, if the *Franck-Condon* factors for these series of compounds followed the same energy gap law [16] (see *Eqn. 3*). This finding is also in accordance with the observation of significant differences in the rate constants of formation of $O_2(^1\Delta_g)$ during O_2 quenching of nπ* and $\pi\pi$* sensitizers, *i.e.*, $k_{\Delta E}^{1\Delta}(n\pi^*) \gg k_{\Delta E}^{1\Delta}(\pi\pi^*)$ [6]. Hence, it is suggested that the *Franck-Condon* factors for the $^{1,3}(T_1(n\pi^*)O_2) \rightarrow {}^{1,3}(S_0(n^2)O_2)$

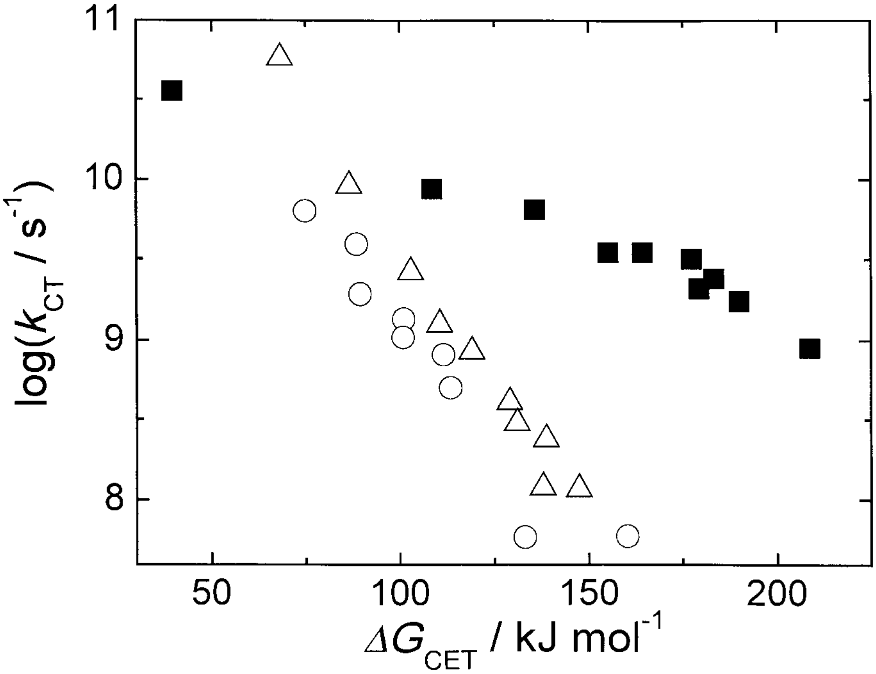


Fig. 2. *Driving-force dependence of the rate constants of CT-induced deactivation of T_1 by $O_2(^3\Sigma_g^-)$, for a series of biphenyl derivatives* (open triangles), *naphthalene derivatives* (open circles), *and benzophenone derivatives* (solid squares) *in TET*

transitions are significantly larger than for the $^{1,3}(T_1(\pi\pi^*)O_2) \rightarrow {}^{1,3}(T_1(\pi^2)O_2)$ nCT transitions in the high excess-energy region.

The reason for this situation may lie in the differences in structure of the complexes formed with nπ^* and $\pi\pi^*$ sensitizers. A deeper insight into the mechanisms of exciplex formation can be gained by an interpretation of the experimental data in terms of *Marcus* electron-transfer theory [27]. Previous work has shown *i*) that the rate constants for the CT-induced processes in both quenching of excited triplet sensitizers by ground-state oxygen, and CT-induced quenching of $O_2(^1\Delta_g)$ by the ground-state sensitizers are best described by a parabolic *Marcus*-type dependence on ΔG_{CET} (*Eqn. 8*), and *ii*) that the fit parameter δ, which was originally introduced as a corrective factor for ΔG_{CET}, gives the best estimates of the average partial charge-transfer character of the exciplexes formed during these processes [12][13]. *Fig. 3* shows the best fits obtained with the benzophenone data of *Tables 4* and *6*, according to *Eqn. 8*. Obviously, the data for both deactivation processes have been treated individually.

Comparative experiments with $O_2(^1\Delta_g)$ quenching are not possible in TET, since the high concentrations required for these experiments could not be reached due to the insufficient solubility of the ketones with low E_{ox} in this solvent. The fit parameters obtained from the plots of *Fig. 3* are: $\delta^2 = 0.278$ and $\lambda = 68.5$ kJ mol^{-1} (A, $O_2(^1\Delta_g)$ deactivation by ground-state benzophenone derivatives in DCM), $\delta^2 = 0.115$ and

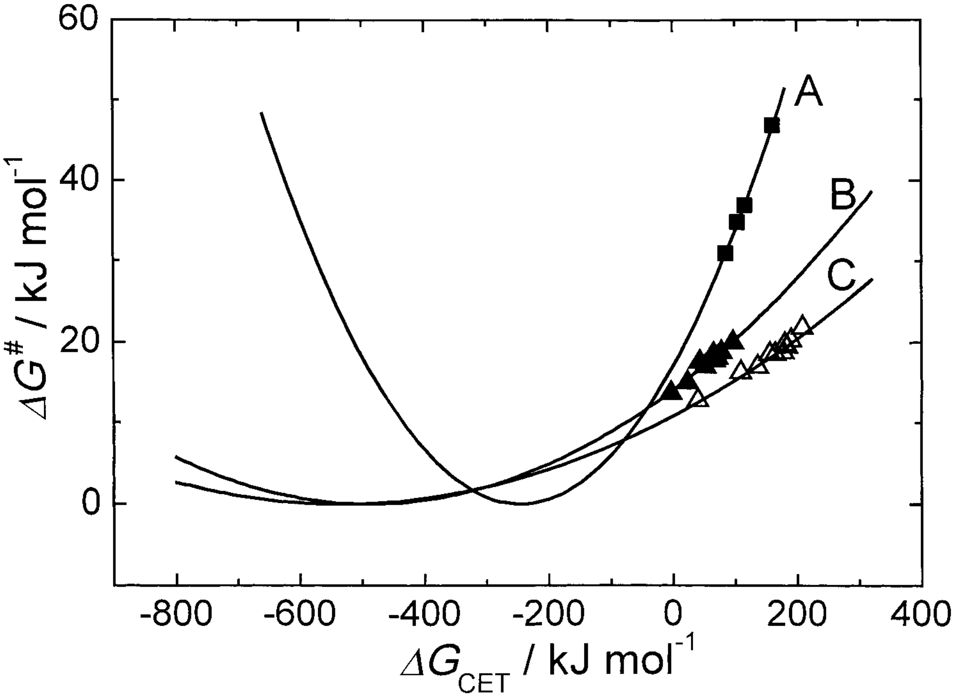


Fig. 3. *Parabolic dependence of* $\Delta G^{\#}$ *on* ΔG_{CET}, *in DCM* (solid symbols) *and TET* (open symbols). Triangles correspond to the deactivation of T_1 by $O_2(^3\Sigma_g^-)$, squares to the deactivation of $O_2(^1\Delta_g)$ by S_0. Lines fit to *Eqn. 8*. For details, see text.

$\lambda = 56.3$ kJ mol^{-1} (B, deactivation of T_1 states of benzophenone derivatives by $O_2(^3\Sigma_g^-)$ in DCM), $\delta^2 = 0.082$ and $\lambda = 44.2$ kJ mol^{-1} (C, deactivation of T_1 states of benzophenone derivatives by $O_2(^3\Sigma_g^-)$ in TET). Reorganization energies are generally described as a sum of two independent contributions,

$$\lambda = \lambda_i + \lambda_o \tag{9}$$

where the λ_i accounts for the reorganization of bond lengths and inner bond angles within the reaction pair, and λ_o describes the energetic requirements for the reorientation of solvent molecules around the reaction pair. All contributions depending on the amount of charge transfer are associated with the latter parameter, which can be calculated by *Eqn. 10*, if the reactants are considered as spheres in a dielectric continuum [28].

$$\lambda_o = \delta^2 e^2 \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_S}\right)\left(\frac{1}{2r^+} + \frac{1}{2r^-} - \frac{1}{r}\right) \tag{10}$$

$r = r^+ + r^-$ is the inter-reactant centre-to-centre distance. The optical dielectric constant ε_{op} of the solvent and is 2.132 in TET and 2.028 in DCM [21]. With the fit parameters above, we calculate the following values: $\lambda_o = 35.6$ kJ mol^{-1} $(O_2(^1\Delta_g)$ deactivation in

DCM), $\lambda_o = 14.7$ kJ mol^{-1} (T_1 deactivation in DCM), and $\lambda_o = 0.6$ kJ mol^{-1} (T_1 deactivation in TET). The separation into intramolecular and solvent contributions to the overall reorganization energies resulting from these calculations is shown in *Fig. 4*.

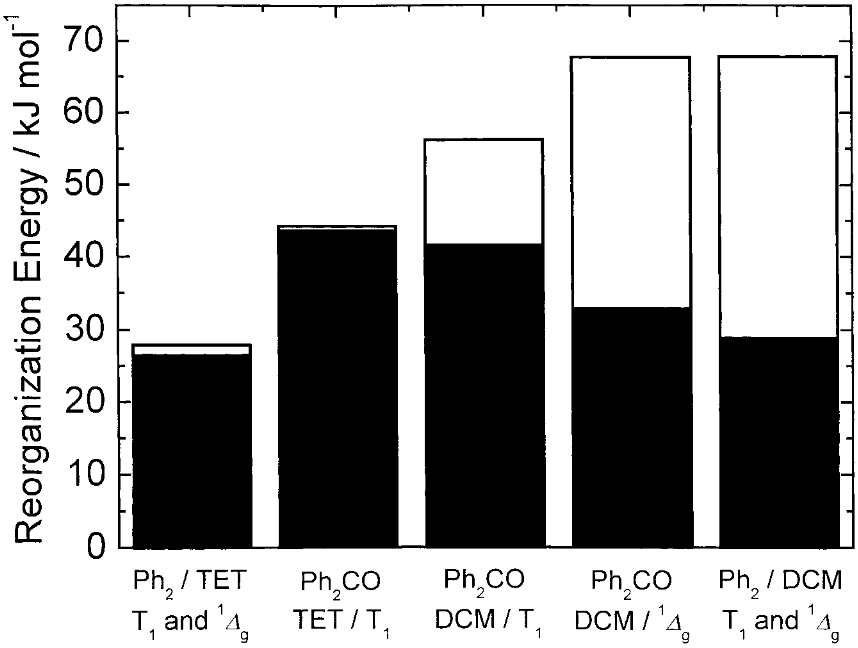
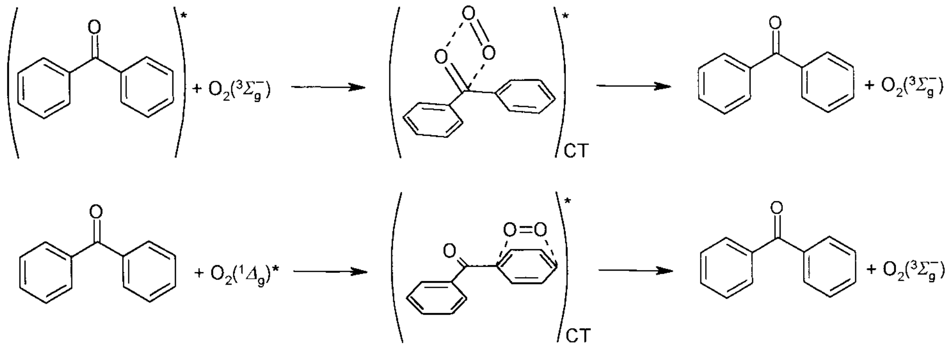


Fig. 4. *Intramolecular* (solid bars) *and solvent* (open bars) *contributions to the reorganization energies observed during quenching of* $O_2(^1\Delta_g)$ *by ground-state benzophenone derivatives in DCM, during quenching of* T_1 *states of benzophenone derivatives by* $O_2(^3\Sigma_g^-)$*, in TET and DCM, and the respective data for a series of biphenyl derivatives, from* [13]

It is very interesting to compare these values with the results previously obtained with a series of biphenyl derivatives [13]. We observe an almost constant value of *ca.* 30 kJ mol^{-1} for the intramolecular reorganization energy $\lambda_i = \lambda - \lambda_o$ of formation of a pCT complex, during *i*) quenching of $\pi\pi^*$ excited biphenyl triplet states by $O_2(^3\Sigma_g^-)$, in TET, DCM, and also ACN (not shown), *ii*) quenching of $O_2(^1\Delta_g)$ by ground-state biphenyl derivatives in the same solvents, and *iii*) quenching of $O_2(^1\Delta_g)$ by ground-state benzophenone derivatives, in DCM. This result suggests that pCT complexes of similar structure are formed during these three processes. In contrast, a significantly larger intramolecular reorganization energy of *ca.* 40 kJ mol^{-1} is observed during oxygen quenching of $n\pi^*$-excited benzophenone triplet states, both in DCM and TET. This means that the complexes formed with $n\pi^*$ excited states involve significantly larger changes in the bond lengths than those formed with $\pi\pi^*$ excited triplets. This is also in accordance with the suggestion of a weaker excess energy dependence of the *Franck-Condon* factors for the deactivation of $^{1,3}(T_1(n\pi^*)O_2)$ complexes compared with the $^{1,3}(T_1(\pi\pi^*)O_2)$ complexes, leading to correspondingly larger rate constants in the high-excess-energy region.

Finally, we may now assess the structure of the complexes formed with molecular oxygen and nπ^* excited benzophenone-derivative triplets, by considering the following: *i*) complexation of $O_2(^3\Sigma_g^-)$ with triplet-excited benzophenone does not occur with the phenyl moieties, *ii*) complexation of $O_2(^3\Sigma_g^-)$ with triplet-excited benzophenone involves significant changes in the bond lengths, and *iii*) the carbonyl group undergoes important dynamics upon excitation of benzophenone, while geometry changes in the rest of the molecule are small or absent [29]. Therefore, the only reasonably arguable structure is a complex where the O_2 molecule is locally bound to the carbonyl group. This contrasts with the situation where O_2 is the initially excited species. Then, complexation occurs with one of the Ph rings. *Scheme 4* illustrates the two structures of exciplexes formed with molecular oxygen and benzophenone.

Scheme 4



A T_1-state-quenching process featuring a local binding of O_2 to the carbonyl group has actually been suggested by *Gorman* and *Rodgers* [2] fifteen years ago. However, these authors proposed a very complicated mechanism, involving the competitive formation of biradicals and trioxetane, to account for the low S_Δ values observed with some ketones. This mechanism has been unequivocally ruled out some years later, on the basis of $^{18}O_2$ quenching experiments with a low-S_Δ ketone [9]. The present results demonstrate that the actual situation is surprisingly simple compared with previous speculations: the deactivation of nπ^* excited triplet ketones occurs by a local interaction of the oxygen molecule with the locally excited ketone carbonyl group, and the formation of a four-center complex involves large geometry changes, compared with the eight-center complex generated during O_2 quenching of $\pi\pi^*$ excited Ph rings. This leads to a large displacement of the potential curve of the $^3(T_1(n\pi^*)^3\Sigma)$ complex with respect to the $^3(S_0(n^2)^3\Sigma)$ complex, which generates comparatively large *Franck-Condon* factors for the $^3(T_1(n\pi^*)^3\Sigma) \rightarrow {}^3(S_0(n^2)^3\Sigma)$ transition.

It has been previously noted that the rate constant of direct formation of $O_2(^1\Delta_g)$, during O_2 quenching of benzophenone, exceeds the value expected for a $^1(T_1(\pi\pi^*)^3\Sigma) \rightarrow {}^1(S_0(\pi^2)^1\Delta)$ nCT transition at the same ΔE by one order of magnitude, whereas no significant effects were observed on the rate constant of formation of $O_2(^1\Sigma_g^+)$ [6]. Together with the presently observed increase by 3–4 orders of magnitude of the rate constant for the deactivation of nπ^* complexes, compared with the value expected for the deactivation of a $\pi\pi^*$ complex at the same ΔE, this shows that the energy-gap law governing the *Franck-Condon* factors for the $(T_1(n\pi^*)O_2) \rightarrow (S_0(n^2)O_2)$ transitions must be rather shallow, compared with the $(T_1(\pi\pi^*)O_2) \rightarrow (S_0(\pi^2)O_2)$ transitions. Hence, the low S_Δ values observed with $n\pi^*$ excited ketones can be explained in a very simple way by such a modified energy-gap law, which leads to relatively high rate constants for the triplet nCT and pCT transition. However, the shape of the energy-gap law is far from being obvious, and also the modified influence of CT interactions can only be understood if the processes leading to formation of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ are analyzed in the same context. This is the subject of ongoing research in our laboratory.

Experimental Part

Benzophenone (*Aldrich*, >99%), 4-methylbenzophenone (*Aldrich*, 99%), 4-methoxybenzophenone (*Aldrich*, 97%), 4,4′-dimethoxybenzophenone (*Lancaster*, >98%), 3,4-dimethylbenzophenone (*Aldrich*, 99%), 4,4′-dichlorobenzophenone (*Lancaster*, 99%), 4-bromobenzophenone (*Aldrich*, 98%), 4-chlorobenzophenone (*Aldrich*, 99%), and 4-cyanobenzophenone (*Lancaster*, 98%) were recrystallized from hexane. 4-Aminobenzophenone (*Merck*, >98%) was recrystallized from Et_2O/EtOH. 4-(Dimethylamino)benzophenone (*Aldrich*, 98%), *Michler*'s ketone (*Aldrich*, 98%), 2,4,6-trimethoxybenzophenone (*Aldrich Rare Chemicals*), 2-aminobenzophenone (*Fluka*, >98%), and tetrabutylammonium hexafluorophosphate (TBAP, *Aldrich*, 98%) were used as received. Phenalenone (*Aldrich*, 97%, CH_2Cl_2/silica gel), and CCl_4 (*Merck*, *p.a.*, Al_2O_3) were purified by column chromatography. CH_2Cl_2 (*Merck*, *p.a.*), and H_2O-free MeCN (*Merck*, *Selectipur*) were used as received. Irradiation was provided by a Q-switched, frequency tripled Nd:YAG laser (*Quantel Brilliant*) at 355 nm or a XeCl-excimer laser (*ATL Lasertechnik*) at 308 nm. The $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ phosphorescence was recorded at 1275 nm with a cryogenic Ge diode (*North Coast EO817P*) and a transient digitizer (*Tektronix TDS 3052*). At least twenty shots were averaged for improved signal-to-noise ratios. In singlet oxygen quenching experiments, solns. of phenalenone were used as sensitizer. $O_2(^1\Delta_g)$ lifetimes were obtained from fits to the first-order decay profiles, and the rate constants for its quenching by the benzophenone derivatives from the slopes of the respective *Stern-Volmer* plots. Rate constants for the oxygen quenching of excited triplet benzophenone derivatives were obtained from the rise of the $O_2(^1\Delta_g \rightarrow {}^3\Sigma_g^-)$ phosphorescence, as described in [30]. Experiments were carried out at r.t., in air-saturated solns., unless otherwise stated. Oxygen concentrations $[O_2]$ are directly proportional to the partial pressure p_{O_2} of O_2. We use for our data the following concentrations $[O_2]_1$ at $p_{O_2} = 1$ bar: 10.7×10^{-3}M (DCM, 20°) and 12.4×10^{-3}M (TET, 20°) [21], and the temp.-dependent vapor pressure p_v, which amounts at 20° to 0.49 bar (DCM), and 0.12 bar (TET) and which has to be evaluated for the actual temp. from respective data collections [31]. Finally, we calculate at atmosheric pressure p_a for air-saturated solutions $[O_2] = [O_2]_1 0.21(p_a - p_v)$. Efficiencies of $O_2(^1\Delta_g)$ generation refer to $S_\Delta = 0.97$ of the reference phenalenone [32]. They were obtained by comparison of excitation-energy-normalized $O_2(^1\Delta_g)$ phosphorescence signals of sample and reference, which were both extrapolated to the time of laser pulse ignition. Triplet energies were determined by phosphorescence spectroscopy. Half-wave oxidation potentials were determined by cyclic voltammetry using the *Bank POS 73* potentioscan. A three-electrode system was employed with a Pt disk as the working electrode, an Ag/AgCl reference electrode and a Pt wire as the counter electrode. All measurements were carried out at r.t., in deoxygenated solns. of H_2O-free MeCN containing 10^{-3} M of the benzophenone derivative and 0.1M TBAP as supporting electrolyte. The voltage scan was 50 mV s^{-1}. In most of the cyclic voltammograms, the reverse reduction peak was absent, indicating a relatively large rate constant of some follow-up reactions of the primarily generated radical cations. Since this fact leads to a shift of the oxidation potential to less positive values, the peak potentials of the voltammograms were taken as approximate thermodynamically relevant oxidation potentials and should be considered as a lower limit.

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REFERENCES

[1] S. K. Chattopadhyay, C. V. Kumar, P. K. Das, *J. Photochem.* **1985**, *30*, 81.

[2] A. A. Gorman, M. A. J. Rodgers, *J. Am. Chem. Soc.* **1986**, *108*, 5074.

[3] R. W. Redmond, S. E. Braslavsky, *Chem. Phys. Lett.* **1988**, *148*, 523.

[4] A. P. Darmanyan, C. S. Foote, *J. Phys. Chem.* **1992**, *96*, 3723.

[5] a) A. P. Darmanyan, C. S. Foote, *J. Phys. Chem.* **1993**, *97*, 4573; b) A. P. Darmanyan, C. S. Foote, *J. Phys. Chem.* **1993**, *97*, 5032.

[6] M. Bodesheim, M. Schütz, R. Schmidt, *Chem. Phys. Lett.* **1994**, *221*, 7.

[7] B. Wang, P. R. Ogilby, *J. Photochem. Photobiol. A: Chem.* **1995**, *90*, 85.

[8] a) J. C. Netto-Ferreira, J. C. Scaiano, *Photochem. Photobiol.* **1991**, *54*, 17; b) M. Terazima, M. Tonooka, T. Azumi, *Photochem. Photobiol.* **1991**, *54*, 59; c) W. M. Nau, J. C. Scaiano, *J. Am. Chem. Soc.* **1996**, *118*, 2742; d) W. M. Nau, J. C. Scaiano, *J. Phys. Chem.* **1996**, *100*, 11360.

[9] J. Bendig, R. Schmidt, H.-D. Brauer, *Chem. Phys. Lett.* **1993**, *202*, 535.

[10] J. M. Aubry, B. Mandard-Cazin, M. Rougee, R. V. Bensasson, *J. Am. Chem. Soc.* **1995**, *117*, 9159.

[11] M. Bobrowski, A. Liwo, S. Oldziej, D. Jeziorek, T. Ossowski, *J. Am. Chem. Soc.* **2000**, *122*, 8112.

[12] C. Schweitzer, Z. Mehrdad, F. Shafii, R. Schmidt, *J. Phys. Chem. A* **2001**, *105*, 5309.

[13] C. Schweitzer, Z. Mehrdad, F. Shafii, R. Schmidt, *Phys. Chem. Chem. Phys.* **2001**, *3*, 3095.

[14] G. Porter, P. Suppan, *Trans. Faraday Soc.* **1965**, *61*, 1664.

[15] A. K. Singh, A. C. Bhasikuttan, D. K. Palit, J. P. Mittal, *J. Phys. Chem. A* **2000**, *104*, 7002.

[16] a) R. Schmidt, F. Shafii, C. Schweitzer, A. A. Abdel-Shafi, F. Wilkinson, *J. Phys. Chem. A* **2001**, *105*, 1811; b) R. Schmidt, F. Shafii, *J. Phys. Chem. A,* in press.

[17] a) A. J. McLean, M. A. J. Rodgers, *J. Am. Chem. Soc.* **1993**, *115*, 4768; b) A. P. Darmanyan, W. Lee, W. S. Jenks, *J. Phys. Chem. A* **1999**, *103*, 2705.

[18] K. Kawaoka, A. U. Khan, D. R. Kearns, *J. Chem. Phys.* **1967**, *46*, 1842.

[19] F. Wilkinson, A. A. Abdel-Shafi, *J. Phys. Chem. A* **1999**, *103*, 5425.

[20] F. Wilkinson, A. A. Abdel-Shafi, *J. Phys. Chem. A* **1997**, *101*, 5509.

[21] S. L. Murov, I. Carmichael, G. L. Hug, 'Handbook of Photochemistry', Marcel Dekker, New York, 1993.

[22] R. Schmidt, E. Afshari, *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 788.

[23] a) K. M. Kadish, M. M. Morrison, *J. Am. Chem. Soc.* **1976**, *98*, 3326; b) H.-K. Leung, G.-Z. Wu, W.-X. Gan, Y.-Y. Chan, *J. Chem. Soc., Chem. Commun.* **1987**, 20.

[24] a) D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, *8*, 259; b) A. Weller, *Z. Phys. Chem., Neue Folge* **1982**, *133*, 93.

[25] S. L. Mattes, S. Farid, in 'Organic Photochemistry', Ed. A. Padwa, Marcel Dekker, New York, 1983, Vol. 6.

[26] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[27] R. A. Marcus, *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

[28] N. Sutin, *Prog. Inorg. Chem.* **1983**, *30*, 441.

[29] S. Kamei, T. Sato, N. Mikami, M. Ito, *J. Phys. Chem.* **1986**, *90*, 5615.

[30] R. Schmidt, M. Bodesheim, *Chem. Phys. Lett.* **1993**, *213*, 111.

[31] 'D'Ans Lax Taschenbuch für Chemiker und Physiker', 3rd ed., Ed. E. Lax, Springer-Verlag, Berlin, 1967, Vol. 1.

[32] a) R. Schmidt, C. Tanielian, R. Dunsbach, C. Wolff, *J. Photochem. Photobiol. A: Chem.* **1994**, *79*, 11; b) E. Oliveros, P. Suardi-Murasecco, T. Aminian-Saghafi, A. M. Braun, H.-J. Hansen, *Helv. Chim. Acta* **1991**, *74*, 79.

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