J. Phys. Chem. A **2004,** *108,* 5509−5513

Deactivation of $O_2(^1\Delta_g)$ Singlet Oxygen by Carotenoids: Internal Conversion of Excited Encounter Complexes

Reinhard Schmidt*

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

Received: March 8, 2004; In Final Form: April 28, 2004

Literature data of rate constants $k_\Delta{}^Q$ of electronic energy transfer (EET) from $O_2(^1\Delta_g)$ singlet oxygen to 28 carotenoids have been analyzed by means of a semiempirical model derived for the deactivation of triplet excited (T_1) molecules by $O_2(^3\Sigma_g{}^-)$ triplet ground-state oxygen. The analysis demonstrates that EET from $O_2(^1\Delta_g)$ to carotenoids occurs not via the electron exchange mechanism according to Dexter but principally via formation of $^1(^1\Delta\cdot S_0)$ encounter complexes that deactivate irreversibly by internal conversion to $^1(T_1\cdot{}^3\Sigma)$ encounter complexes leading to formation of the T_1 excited carotenoid. The dependence of $\log(k_\Delta{}^Q)$ on the excess energy of the EET process is quantitatively described. The results indicate that EET processes to and from O_2 could generally occur via IC of excited complexes.

1. Introduction

Carotenoids are a widespread class of compounds attracting continuous interest because of their important role in photobiology, photochemistry, and photomedicine.[1−4] Their antioxidant effect rests in part on their capability of very efficient deactivation of the cytotoxic singlet oxygen $O_2(^1\Delta_g)$. Foote and Denny observed as first physical quenching of $O_2(^1\Delta_g)$ by β-carotene, suggesting an electronic energy transfer (EET) mechanism for this process.[5] Farmilo and Wilkinson determined the rate constant of $O_2(^1\Delta_g)$ quenching by β-carotene to $k_\Delta{}^Q = 1.3 \times 10^{10}$ M^{-1} s^{-1} in benzene.[6] They furthermore demonstrated that quenching is accompanied by population of the β-carotene triplet state T_1 confirming that the spin-allowed EET process of eq 1 takes place, where $O_2(^3\Sigma_g{}^-)$ and S_0 represent triplet ground-state oxygen and singlet ground-state quencher.

$$O_2(^1\Delta_g) + S_0 \rightarrow O_2(^3\Sigma_g{}^-) + T_1 \qquad (1)$$

Effective EET deactivation by carotenoids is only observed if this process demands negligible thermal activation. Already Foote et al.[7] found that the values of $k_\Delta{}^Q$ strongly decrease, if the number of conjugated double bonds gets smaller than $N = 11$ for β-carotene. This was attributed to an increase of the quencher triplet-state energy E_T to values significantly above the excitation energy E_Δ of $O_2(^1\Delta_g)$. The value of E_T of β-carotene is close to the value of E_Δ. Lambert and Redmond measured $E_T = 81$ kJ mol^{-1} by photoacoustic calorimetry in benzene, and Truscott and co-workers obtained $E_T = 88$ kJ mol^{-1} by phosphorescence measurements in C_6D_6.[8,9] These values correspond to the relaxed triplet state.[8] A significantly higher energy was determined by Gorman et al. in variable-temperature experiments of the quenching of $O_2(^1\Delta_g)$ by β-carotene in toluene.[10] Their results placed the spectroscopic triplet energy level 1.5 kJ mol^{-1} above the $O_2(^1\Delta_g)$ energy, which amounts in that solvent to $E_\Delta = 93.8$ kJ mol^{-1}.[11] Thus, $E_T = 95$ kJ mol^{-1} is valid if β-carotene is the quencher. The average value $E_T = 85$ kJ mol^{-1} of the relaxed triplet is only relevant if triplet β-carotene acts as energy donor. These results are in accordance with the lack of $O_2(^1\Delta_g)$ formation in the quenching of T_1 excited β-carotene by oxygen.[8]

Rate constants $k_\Delta{}^Q$ of the deactivation by carotenoids have been determined by several groups using in part different techniques. An overall consistent picture was obtained.[1] Values $0.6 \times 10^{10} \le k_\Delta{}^Q \le 1.4 \times 10^{10}$ M^{-1} s^{-1} have been measured with β-carotene in solvents of different polarity.[2,6,10,12−14] Smaller rate constants have only been found in protic solvents where aggregation of the quencher was assumed.[15] The rate constants of other carotenoids with $N \ge 11$ are of similar magnitude. Furthermore, no relationship was found between $k_\Delta{}^Q$ and the nature of the end groups of the carotenoid.[15,16] Comparison with the diffusion-controlled rate constant k_d soon demonstrated that with only very few exceptions $k_\Delta{}^Q$ is 2- to 3-fold smaller than k_d.[10,13,15] This was further corroborated in a detailed investigation of the influence of solvent on $k_\Delta{}^Q$ performed by Conn et al. with β-carotene and lycopene,[14] where only a very slight decrease of $k_\Delta{}^Q$ with solvent viscosity η was observed, much weaker than expected for k_d. Thus, the spin-allowed exothermic EET process of eq 1 is not diffusion-controlled like other deactivation processes following the electron exchange mechanism described by Dexter. This is an at first sight rather surprising and hitherto actually not understood result, although it was speculated that this could be due to an orbital statistical factor of 0.5 arising out of the 2-fold degeneracy of the $^1\Delta_g$ state of $O_2(^1\Delta_g)$.[10]

The reasons for the unexpected slow EET deactivation of $O_2(^1\Delta_g)$ are, however, different. It is important to note that the quenching of triplet states T_1 by $O_2(^3\Sigma_g{}^-)$ leading to S_0 and $O_2(^1\Delta_g)$, which is formally the back-reaction of process 1, also proceeds with relatively small rate constants. It will be shown that the rules derived in the detailed investigation of the quenching of $T_1(\pi\pi^*)$ excited molecules by $O_2(^3\Sigma_g{}^-)$ in our laboratory provide the key for understanding the mechanism of EET deactivation of $O_2(^1\Delta_g)$.[17−21] To this end, we will analyze an immensely valuable data set on the deactivation of $O_2(^1\Delta_g)$ by carotenoids published by the groups of Martin and

---

* Fax: (+49)69-798-29445. E-mail: R.Schmidt@chemie.uni-frankfurt.de.

10.1021/jp048958u CCC: $27.50

TABLE 1: Singlet-State Energy E_S and Rate Constant $k_\Delta{}^Q$ of $O_2(^1\Delta_g)$ Deactivation by Carotenoids (Data and Notation of Martin, Sies, and Co-workers[22])

carotenoid	E_S/ (kJ mol^{-1})	$k_\Delta{}^Q$/ (10^9 M^{-1} s^{-1})	carotenoid	E_S/ (kJ mol^{-1})	$k_\Delta{}^Q$/ (10^9 M^{-1} s^{-1})
16d	273.0	0.2	16b	237.8	12.4
4d	271.9	0.5	9b	236.8	11.1
12d	270.5	0.1	7b	236.8	12.7
11c	267.5	3.0	15	234.5	11.0
10c	266.3	1.6	4b	233.6	12.0
1b	260.0	8.4	1a	231.8	13.3
16c	252.8	8.1	5b	230.5	12.6
14b	247.1	8.8	16a	229.2	12.9
2b	246.0	10.2	3a	226.5	13.0
13b	245.5	8.4	12b	224.8	11.7
12c	245.1	10.2	4a	217.4	13.8
3b	245.1	9.0	6b	216.7	12.7
10b	243.6	9.0	5a	215.9	12.3
11b	239.7	11.1	8b	204.8	12.1

Sies.[22] Hereby we will realize that the same energy gap relation determines the excess energy dependence of the rate constants of both quenching processes.

2. Data

Quenching of $O_2(^1\Delta_g)$ by Carotenoids. Martin, Sies, and co-workers performed the most comprising investigation of the quenching of $O_2(^1\Delta_g)$ by carotenoids. They determined with one single and reliable method rate constants $k_\Delta{}^Q$ for the large number of 28 carotenoids, with various end groups and a significant variation in the number of conjugated double bonds ($6 \leq N \leq 17$) in the solvent mixture $C_2H_5OH/CHCl_3/D_2O$ (50:50:1) at 37 °C.[22] Thus, the carotenoid is the only variable of this data set. The $k_\Delta{}^Q$ data are listed in Table 1 together with the compound notation used by Martin, Sies, and co-workers and the corresponding energy E_S of the longest wavelength $\pi\pi^*$ absorption. Rate constants $k_\Delta{}^Q$ strongly increase with the decreasing value of E_S to approach a limiting value of $k_\Delta{}^Q \approx 1.2 \times 10^{10}$ M^{-1} s^{-1} at $E_S \lesssim 240$ kJ mol^{-1}, which was assumed to be equal to k_d.[22]

However, the diffusion-controlled rate constant for reactions with O_2 is larger in that environment. Wilkinson and Abdel-Shafi[23] found in a careful investigation of rate constants $k_S{}^Q$ of fluorescence quenching by O_2 that the maximum values of $k_S{}^Q$ corresponding to k_d amount at 25 °C to 4.50×10^{10} M^{-1} s^{-1} in CH_3CN ($\eta = 0.341$ mPa s at 25 °C),[24] 3.33×10^{10} M^{-1} s^{-1} in C_6H_6 ($\eta = 0.603$ mPa s),[24] and 2.72×10^{10} M^{-1} s^{-1} in C_6H_{12} ($\eta = 0.898$ mPa s).[24] Okamoto derived in temperature- and pressure-dependent investigations of the diffusion-controlled quenching of the florescence of 9-methylanthracene by O_2 the empirical linear relation 2 with coefficients $b \approx 4/3$ and $c \approx 2/3$.[25]

$$\ln(k_d) = a + b\ln(T) - c\ln(\eta) \tag{2}$$

The fit of eq 2 to the above three data pairs results in $a + b\ln(298) = 23.97$ and $c = 0.521$, allowing the interpolation of k_d for reactions with O_2 for liquids of different viscosity and temperature. Values of 4.49×10^{10} (CH_3CN), 3.34×10^{10} (C_6H_6), and 2.71×10^{10} M^{-1} s^{-1} (C_6H_{12}) are obtained with that fit and the given values of η, proving the validity of eq 2 at 298 K. However, the data of Martin, Sies, and co-workers have been measured in a solvent mixture and at the slightly higher temperature of 310 K. Literature data of viscosities of solvent mixtures of C_2H_5OH and $CHCl_3$ at various temperatures demonstrate excellent linear variations of $\eta = f(x_{EtOH})$ with the mole fraction x_{EtOH} of C_2H_5OH up to $x_{EtOH} = 0.755$.[26] The linear fit of $\eta_{310} = f(x_{EtOH})$ interpolated from data measured at 303 and 313 K to 310 K versus x_{EtOH} results in $\eta_{310} = 0.475 + 0.523x_{EtOH}$ mPa s. Thus, $\eta_{310} = 0.777$ mPa s is obtained for the 50:50 mixture $C_2H_5OH/CHCl_3$ ($x_{EtOH} = 0.578$) leading with $a + b\ln(298) = 23.97$ and $c = 0.521$ to $k_d = 2.93 \times 10^{10}$ M^{-1} s^{-1}. Considering the additional variation of k_d due to the small temperature increase by multiplying with $(310/298)^{4/3}$, see eq 2, yields finally $k_d = 3.1 \times 10^{10}$ M^{-1} s^{-1} for that binary mixture at 37 °C. This value of k_d is assumed to be also valid for the ternary solvent mixture $C_2H_5OH/CHCl_3/D_2O$ (50:50:1) actually investigated. Thus, the limiting value of $k_\Delta{}^Q$ is about 2.6 times smaller than k_d.

Quenching of Excited Triplet States by Ground-State Oxygen. The quenching of triplet states T_1 by $O_2(^3\Sigma_g{}^-)$ proceeds with overall rate constants $k_T{}^Q$ also smaller than k_d.[1] Hereby processes 3−5 compete for $E_T > E_\Sigma = 157$ kJ mol^{-1}, the excitation energy of the second excited singlet oxygen $O_2(^1\Sigma_g{}^+)$.

$$T_1 + O_2(^3\Sigma_g{}^-) \rightarrow S_0 + O_2(^1\Sigma_g{}^+) \tag{3}$$

$$T_1 + O_2(^3\Sigma_g{}^-) \rightarrow S_0 + O_2(^1\Delta_g) \tag{4}$$

$$T_1 + O_2(^3\Sigma_g{}^-) \rightarrow S_0 + O_2(^3\Sigma_g{}^-) \tag{5}$$

In the initial step of reaction T_1 and $O_2(^3\Sigma_g{}^-)$ form encounter complexes $^m(T_1{\cdot}{}^3\Sigma)$ of singlet, triplet, and quintet multiplicity ($m = 1, 3, 5$). No forward reaction channel exists for the $^5(T_1{\cdot}{}^3\Sigma)$ encounter complex. The $^{1,3}(T_1{\cdot}{}^3\Sigma)$ complexes react in forward direction producing S_0 and $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, or $O_2(^3\Sigma_g{}^-)$ with overall rate constant k_D. k_D was calculated with eq 6, where $k_{-d} = k_d/\mathrm{M}^{-1}$ represents the rate constant of back-dissociation of the encounter complexes to T_1 and $O_2(^3\Sigma_g{}^-)$ with unit s^{-1}.[18]

$$k_D = k_{-d}k_T{}^Q/(k_d - k_T{}^Q) \tag{6}$$

Recently, we demonstrated how to split the overall rate constant k_D into the single rate constants $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$ of formation of $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$.[27,28] We applied this technique to one series of $\pi\pi^*$ triplet sensitizers of different molecular structure and strongly varying E_T,[17] and to three different homologous series of $\pi\pi^*$ triplet sensitizers with in each series almost constant E_T but strongly varying oxidation potential E_{ox}.[18−20] Hereby we discovered that $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ are directly produced by internal conversion (IC) of $^{1,3}(T_1{\cdot}{}^3\Sigma)$ encounter complexes with negligible CT interactions (nCT complexes) and indirectly via the reaction of $^{1,3}(T_1{\cdot}{}^3\Sigma)$ encounter complexes to $^{1,3}(T_1{\cdot}{}^3\Sigma)$ exciplexes with partial CT character (pCT complexes) followed by IC to lower exciplex states. The overall rate constants of each product channel, i.e., $k_T{}^{1\Sigma}$, $k_T{}^{1\Delta}$, and $k_T{}^{3\Sigma}$ ($=k_T{}^P$) was shown to be additively composed of rate constants of IC of nCT complexes ($k_{\Delta E}{}^P$) and of pCT complex formation ($k_{CT}{}^P$).[18−20]

For $^{1,3}(T_1{\cdot}{}^3\Sigma)$ nCT complexes three different IC processes to lower complex states compete, yielding $O_2(^1\Sigma_g{}^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g{}^-)$ by subsequent complex dissociation: $^1(T_1{\cdot}{}^3\Sigma) \rightarrow {}^1(S_0{\cdot}{}^1\Sigma) \rightarrow S_0 + O_2(^1\Sigma_g{}^+)$, $^1(T_1{\cdot}{}^3\Sigma) \rightarrow {}^1(S_0{\cdot}{}^1\Delta) \rightarrow S_0 + O_2(^1\Delta_g)$, and $^3(T_1{\cdot}{}^3\Sigma) \rightarrow {}^3(S_0{\cdot}{}^3\Sigma) \rightarrow S_0 + O_2(^3\Sigma_g{}^-)$. Since the logarithms of the multiplicity normalized rate constants $k_{\Delta E}{}^{1\Sigma}$, $k_{\Delta E}{}^{1\Delta}$, and $k_{\Delta E}{}^{3\Sigma}/3$ ($=k_{\Delta E}{}^P/m$) follow a common dependence on the respective excess energy ΔE ($\Delta E_{1\Sigma} = E_T - E_\Sigma$, $\Delta E_{1\Delta} = E_T - E_\Delta$, and $\Delta E_{3\Sigma} = E_T$), it was concluded that a fully established spin-statistical equilibrium exists between $^m(T_1{\cdot}{}^3\Sigma)$ nCT complexes of different multiplicity.[18] The empirical energy gap relation $\log(k_{\Delta E}{}^P/m) = f(\Delta E)$ of eq 7 resulting from

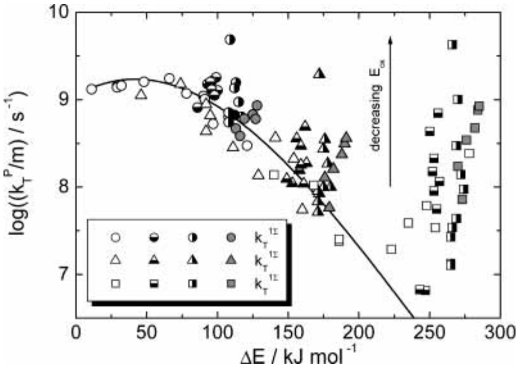

Figure 1. Dependence of $\log(k_T^P/m)$ on the excess energy ΔE. Data of a series of sensitizers of differing structure with a wide variation of E_T (open symbols), of naphthalenes (lower half filled symbols), of biphenyls (right half filled symbols), and of fluorenes (gray filled symbols). The curve represents the empirical energy gap relation $\log(k_{\Delta E}^P/m)$ of eq 7.[17−20]

deactivation of $T_1(\pi\pi^*)$ is drawn as a curve in Figure 1 and describes the smaller values of $\log(k_T^P/m)$ for each oxygen product state.

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

The modification of naphthalene, biphenyl, and fluorene by substituents with different electron-donating or -withdrawing properties leads to compounds with strongly varying oxidation potential E_{ox}. However, E_T remains almost constant in each of the three series. Experiments with triplet sensitizers of these homologous series showed that the overall rate constants k_T^P increase at a given excess energy ΔE with decreasing value of E_{ox} (see Figure 1),[18−20] i.e., with increasing CT interactions due to the opening of the second deactivation channel via $^{1,3}(T_1{\cdot}^3\Sigma)$ pCT complexes.[18−20,23,29,30] The CT interactions can be quantified by the free energy change ΔG_{CET} for complete electron transfer from the T_1 excited sensitizer to O_2 according to eq 8.[31]

$$\Delta G_{CET} = F(E_{ox} - E_{red}) - E_{exc} + C \quad (8)$$

F and E_{red} represent Faraday's constant and the reduction potential of the electron acceptor (for O_2 −0.78 V vs SCE in acetonitrile),[32] $E_{exc} = E_T$ for T_1 state quenching, and C is the electrostatic interaction energy, which is inversely proportional to the dielectric constant and is usually taken as $C = 0$ in acetonitrile. During the investigation of 45 $\pi\pi^*$ triplet sensitizers in CCl_4, it was shown that the rate constants k_{CT}^P/m of formation of $^{1,3}(T_1{\cdot}^3\Sigma)$ exciplexes, producing $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ in the pCT deactivation channel via IC, can be calculated by the empirical linear relationship of eq 9.[21,33]

$$\log(k_{CT}^P/m) = \log(c^P/m) + 7.65 - 0.023\Delta G_{CET} \quad (9)$$

Hereby, different statistical weights c^P correspond to the singlet and triplet O_2 product states; i.e., c^P stands for $c^{1\Sigma} + c^{1\Delta} = 1$ and $c^{3\Sigma} = 3$, respectively.

3. Discussion

The rate constant of exchange energy transfer according to Dexter is proportional to the overlap integral between the normalized donor emission and acceptor absorption spectra.[34] Because of the very narrow spectra of the 0−0 transitions of the $O_2(^1\Sigma_g^+) \leftarrow O_2(^3\Sigma_g^-)$ absorption at 765 (spectral half-width $\Delta\lambda_{1/2} \approx 10$ nm) and the $O_2(^1\Delta_g) \leftarrow O_2(^3\Sigma_g^-)$ absorption at 1275 nm ($\Delta\lambda_{1/2} \approx 15$ nm),[1] only very small overlap integrals result for the triplet sensitization of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$. On the basis of estimates of the ratio of corresponding overlap integrals, we recently concluded that $k_T^{1\Sigma}/k_T^{1\Delta} \geq 500$ should hold true if exchange energy transfer would be the mechanism of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ sensitzation.[18] However, $k_T^{1\Sigma}/k_T^{1\Delta} \lesssim 10$ was experimentally found, as can be seen exemplarily from the naphthalene, biphenyl, and fluorene data of Figure 1. This result excludes the Dexter mechanism as principal EET mechanism for T_1 state quenching by $O_2(^3\Sigma_g^-)$. It was concluded that $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ are formed by IC of $^{1,3}(T_1{\cdot}^3\Sigma)$ complexes.

Since $\Delta\lambda_{1/2} \approx 15$ nm is also valid for the $O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-)$ emission spectrum,[11] it seems likely that similarly to T_1 state quenching by $O_2(^3\Sigma_g^-)$ EET deactivation of $O_2(^1\Delta_g)$ occurs also mainly by the IC of intermediate $^1(^1\Delta{\cdot}S_0)$ complexes but not by the electron exchange mechanism. The singlet $^1(^1\Delta{\cdot}S_0)$ encounter complex is formed from $O_2(^1\Delta_g)$ and singlet ground-state quencher with spin-statistical weight 1 and rate constant k_d in the first step of reaction 10.

$$O_2(^1\Delta_g) + S_0 \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} {}^1(^1\Delta{\cdot}S_0) \xrightarrow{k_{IC}} {}^1(T_1{\cdot}^3\Sigma) \rightarrow T_1 + O_2(^3\Sigma_g^-) \quad (10)$$

$^1(^1\Delta{\cdot}S_0)$ either decays with k_{-d} back to $O_2(^1\Delta_g)$ and S_0 or deactivates by IC with rate constant k_{IC} to the $^1(T_1{\cdot}^3\Sigma)$ complex state producing finally T_1 and $O_2(^3\Sigma_g^-)$. Intersystem crossing $^1(^1\Delta{\cdot}S_0) \rightarrow {}^3(T_1{\cdot}^3\Sigma)$ with subsequent IC to $^3(S_0{\cdot}^3\Sigma)$ is forbidden. Therefore, T_1 and $O_2(^3\Sigma_g^-)$ should be the principal products of the physical deactivation of $^1(^1\Delta{\cdot}S_0)$ complexes. If CT interactions between $O_2(^1\Delta_g)$ and quencher are negligible, only IC $^1(^1\Delta{\cdot}S_0) \rightarrow {}^1(T_1{\cdot}^3\Sigma)$ of nCT complexes contributes to EET deactivation. In that case the energy gap relation $\log(k_{\Delta E}^P/m) = f(\Delta E)$ of eq 7 should also be valid for the excess energy dependence of the rate constant of IC of $^1(^1\Delta{\cdot}S_0)$ nCT complexes with $\Delta E = E_\Delta - E_T$. Hereby, we have only to consider that eq 7 yields rate constants normalized to the IC of $^1(T_1{\cdot}^3\Sigma)$ nCT complexes. However, their spin-statistical weight among the $^{1,3,5}(T_1{\cdot}^3\Sigma)$ nCT complexes amounts to only 1/9. Thus, $k_{\Delta E}^P/m$ calculated via eq 7 has to be multiplied by the factor 9 to obtain k_{IC} corresponding to IC $^1(^1\Delta{\cdot}S_0) \rightarrow {}^1(T_1{\cdot}^3\Sigma)$ of nCT complexes. Since the resulting values of $k_{IC} = 9(k_{\Delta E}^P/m)$ are for $\Delta E \gtrsim 0$ kJ mol^{-1} not far from the diffusion-controlled limit, the experimentally measurable rate constants k_Δ^Q are obtained with eq 11.

$$k_\Delta^Q = 9k_d(k_{\Delta E}^P/m)/(k_{-d} + 9(k_{\Delta E}^P/m)) \quad (11)$$

Deviations to larger rate constants could be expected if CT interactions between ground-state quencher and oxygen become effective leading to formation of $^1(^1\Delta{\cdot}S_0)$ exciplexes from $^1(^1\Delta{\cdot}S_0)$ encounter complexes opening a CT induced deactivation path similarly to T_1 state quenching by $O_2(^3\Sigma_g^-)$; see Figure 1. The CT interactions are quantified by ΔG_{CET}, which is calculated with eq 8 with $E_{exc} = E_\Delta$. The first oxidation potential has recently been determined for β-carotene to $E_{ox} = 0.540$ V vs SCE in CH_2Cl_2.[35] Taking this value to be compatible with redox potentials determined in acetonitrile, we estimate $\Delta G_{CET} = 33$ kJ mol^{-1}. The nCT path dominates in the deactivation of T_1 excited molecules by $O_2(^3\Sigma_g^-)$ in the nonpolar solvent CCl_4 if $\Delta G_{CET} \gtrsim 50$ kJ mol^{-1}.[21,33] Assuming that this result can directly be transferred to EET deactivation of $O_2(^1\Delta_g)$, it appears that CT enhanced deactivation by reaction of $^1(^1\Delta{\cdot}S_0)$ encounter complexes to $^1(^1\Delta{\cdot}S_0)$ exciplexes with subsequent IC $^1(^1\Delta{\cdot}S_0) \rightarrow {}^1(T_1{\cdot}^3\Sigma)$ is of little importance for β-carotene in a nonpolar environment. Actually, eq 9 yields only the small rate constant of exciplex formation of $k_{CT}{}^P/m \approx 8 \times 10^6\ s^{-1}$. Considering again the 9-fold higher statistical weight of $^1(^1\Delta{\cdot}S_0)$ complexes yields $9(k_{CT}{}^P/m) \approx 8 \times 10^7\ s^{-1}$. This result is only about 1% of $9(k_{\Delta E}{}^P/m) \approx 1 \times 10^{10}\ s^{-1}$ calculated with $\Delta E \gtrsim 0$ kJ mol^{-1} with eq 7. The CT contribution to the overall deactivation rate constant of T_1 by $O_2(^3\Sigma_g{}^-)$ increases, however, significantly with solvent polarity. For example, Wilkinson and Abdel-Shafi found for biphenyls with $\Delta G_{CET} \lesssim -23$ kJ mol^{-1}, for which pCT deactivation dominates, a 4-fold increase in going from cyclohexane to acetonitrile.[23] Therefore, it can a priori not be excluded that additional CT induced EET deactivation of $O_2(^1\Delta_g)$ takes place in the polar solvent mixture used by Martin, Sies, and co-workers for some carotenoids with lower oxidation potentials than that of β-carotene.

As discussed above, spectroscopic triplet energies of the carotenoids are required for the analysis of the rate constants $k_\Delta{}^Q$ of $O_2(^1\Delta_g)$ deactivation. Unfortunately, this value is only known for β-carotene, where $E_T = 95$ kJ mol^{-1} is by about 1 kJ mol^{-1} larger than E_Δ.[36] Thus, an excited-state equilibrium $^1(^1\Delta{\cdot}S_0) \rightleftharpoons {}^1(T_1{\cdot}^3\Sigma)$ could be established during the deactivation process as it was actually found by Rodgers and co-workers in the quenching of T_1 excited naphthalocyanines by $O_2(^3\Sigma_g{}^-)$.[37] However, in the latter cases the difference between spectroscopic and relaxed-state energies of $O_2(^1\Delta_g)$ are only about 0.4 kJ mol^{-1},[38] in contrast to T_1 excited β-carotene where this difference amounts to about 10 kJ mol^{-1}. Therefore, it is assumed that once IC $^1(^1\Delta{\cdot}S_0) \rightarrow {}^1(T_1{\cdot}^3\Sigma)$ has taken place, this energy difference is very rapidly released as heat in the reorientation of the flexible polyene chain. Thus, EET deactivation of $O_2(^1\Delta_g)$ by carotenoids should be irreversible, even if it is slightly endothermic. For necessary thermal activation in endothermic EET ($\Delta E < 0$) one can therefore account by simply multiplying $9(k_{\Delta E}{}^P/m)$ derived via eq 7 with the Boltzmann weighting factor $\exp(-|\Delta E|/(RT))$. However, alternatively also reversible EET will be considered. For that case the corresponding weighting factor was given by Sandros as $\exp(\Delta E/(RT))/\{1 + \exp(\Delta E/(RT))\}$.[39]

Due to the lack of experimental spectroscopic triplet energies of carotenoids, these data have to be estimated. To this end Martin, Sies, and co-workers analyzed the dependence of the lowest singlet−singlet $\pi\pi^*$ excitation energy E_S on the effective chain length of the carotenoid and suggested the proportionality of E_T to E_S.[22] Since they found an approximately linear decrease of $\log(k_\Delta{}^Q)$ with increasing E_S in the endothermic region with slope $-(2.3 \times R \times 310)^{-1}$, they concluded that the relation $E_T = E_S - 172$ kJ mol^{-1} with slope 1, calibrated by the *relaxed triplet* energy $E_T = 88$ kJ mol^{-1} of β-carotene,[9] could hold true for the investigated carotenoids. Figure 2 displays a corresponding plot of $\log(k_\Delta{}^Q)$ versus the excess energy $\Delta E = E_\Delta - E_T$ estimated with $E_T = E_S - 165$ kJ mol^{-1}, calibrated by the value of $E_T = 95$ kJ mol^{-1} of the *spectroscopic energy* level of β-carotene.

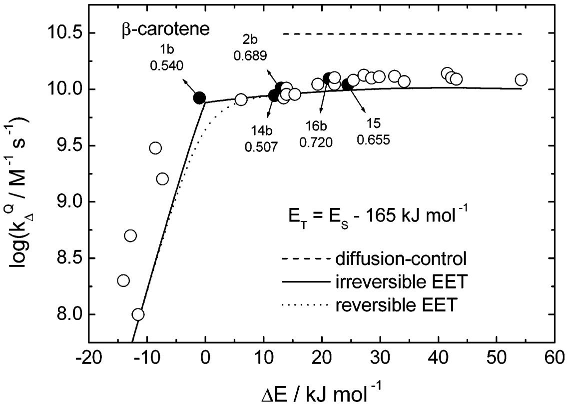

Figure 2. Dependence of $\log(k_\Delta{}^Q)$ on the excess energy ΔE estimated with $E_T = E_S - 165$ kJ mol^{-1}. $k_\Delta{}^Q$ data of Martin, Sies, and co-workers; see Table 1.[22] The solid circles correspond to carotenoids indicated by the corresponding number and oxidation potential.[35] The dashed line indicates the diffusion-controlled limit, the solid line represents the excess energy dependence of irreversible EET, and the dotted line results for reversible EET.

The dashed line parallel to the abscissa shown in Figure 2 corresponds to $\log(k_d)$. Even the largest experimental values of $\log(k_\Delta{}^Q)$ are distinctly smaller than the diffusion-controlled limit underlining the nondiffusional character of the EET process. The experimental data are rather well described by the curve drawn as a solid line, calculated with eqs 7 and 11 assuming irreversible energy transfer. For higher excess energies a systematic deviation of $\log(k_\Delta{}^Q)$ from the calculated curve has to be noted, which, however, is small. The deviation of the 15 experimental $k_\Delta{}^Q$ data with the highest excess energies ΔE amounts to only $+30 \pm 8\%$ compared with the calculated values. This deviation could be the consequence of the neglect of CT interactions and should be more important for the carotenoids with even smaller oxidation potential than β-carotene.

Recently Kispert and co-workers determined oxidation potentials of 12 natural carotenoids.[35] Five of them have also been used as quenchers in the study of Martin, Sies, and co-workers discussed here: β-carotene, **1b**; lycopene, **14b**; canthaxanthin, **2b**; 8′-apo-β-caroten-8′-al, **16b**; and rhodoxanthin, **15**.[22] The corresponding $\log(k_\Delta{}^Q)$ data are indicated as solid circles and given with notation and the respective first oxidation potentials (V vs SCE in CH_2Cl_2)[35] in Figure 2. These data demonstrate that CT enhanced EET deactivation of $O_2(^1\Delta_g)$ by carotenoids is not important. The $\log(k_\Delta{}^Q)$ value of lycopene, having the lowest oxidation potential, does not deviate to larger values but is intersected by the calculated curve. In contrast $\log(k_\Delta{}^Q)$ is by 35% larger than calculated for 8′-apo-β-caroten-8′-al, although it has the highest value of E_{ox}. Thus, the small but systematic deviation of the experimental $\log(k_\Delta{}^Q)$ data is most probably the consequence of transferring an empirical energy gap relation derived for the IC of $^{1,3}(T_1{\cdot}^3\Sigma)$ encounter complexes with aromatic T_1 excited molecules to the IC of $^1(^1\Delta{\cdot}S_0)$ encounter complexes with long-chain polyene molecules.

The still close agreement between the experimental data and the calculated curve is striking, especially if it is considered that the calculation rests on a model derived for EET quenching of T_1 excited molecules by $O_2(^3\Sigma_g{}^-)$. The weak excess energy dependence of the function $\log(k_{\Delta E}{}^P/m)$ of eq 7 in the $0 \lesssim \Delta E \lesssim 50$ kJ mol^{-1} range (see Figure 1) certainly contributes to the good description of the data in the exothermic region, since in that case errors in the estimation of E_T cause only horizontal but no vertical shifts of the $\log(k_\Delta{}^Q)$ data of Figure 2.

Due to the use of the Boltzmann weighting factor the calculated curve rises in the endothermic region ($\Delta E < 0$) with slope $(2.3 \times R \times 310)^{-1}$, similarly to the experimental data. However, it has to be noted that the curve does not intersect but rather is parallel to the $\log(k_{\Delta E}{}^P/m)$ data. Since ΔE is accurately known only for β-carotene with $\Delta E = -1$ kJ mol^{-1}, this mismatch could be the consequence of an imperfect E_T estimation for the five carotenoids with the highest values of E_S resulting in large triplet energies.

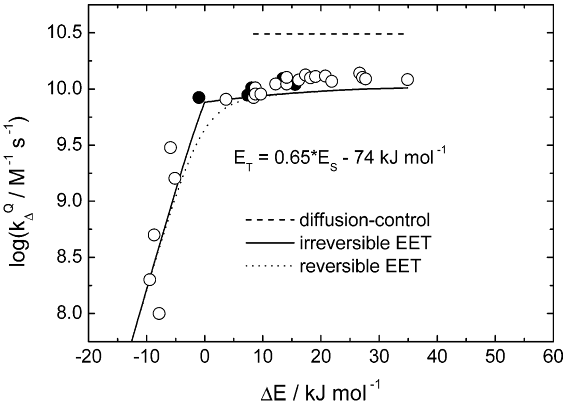

Figure 3. Dependence of $\log(k_\Delta^Q)$ on the excess energy ΔE estimated with $E_T = 0.65E_S - 74$ kJ mol^{-1}. k_Δ^Q data of Martin, Sies, and coworkers; see Table 1.[22] The dashed line indicates the diffusion-controlled limit, the solid line represents irreversible EET, and the dotted line represents reversible EET. The solid circles correspond to the five carotenoids indicated in Figure 2.

Finally, Figure 2 displays as a dotted curve the calculation based on the assumption of reversible EET with the $^1(^1\Delta{\cdot}S_0) \rightleftharpoons {}^1(T_1{\cdot}^3\Sigma)$ excited-state equilibrium. This curve misses the β-carotene value and describes the experimental data in the endothermic region worse. Thus, EET to carotenoids is irreversible, in agreement with the above-made conclusions.

The relation $E_T = E_S - 165$ kJ mol^{-1} used for estimation of ΔE is a rough approximation selected mainly because of the approximately linear decrease of $\log(k_\Delta^Q)$ with E_S with slope $-(2.3 \times R \times 310)^{-1}$ in the endothermic region of EET.[22] A physically more meaningful relation could eventually be obtained making the reasonable assumption of a proportional decrease of the S_1-T_1 energy gap with decreasing S_1 energy instead of keeping $E_S - E_T = 165$ kJ mol^{-1} constant in the $273.0 \geq E_S \geq 239.7$ kJ mol^{-1} range. This condition is met by the relation $E_T = 0.65E_S - 74$ kJ mol^{-1}, again calibrated by $E_T = 95$ kJ mol^{-1} of β-carotene. This alternative but still crude approximation has been used to estimate the excess energies for the plot of $\log(k_\Delta^Q)$ versus ΔE shown in Figure 3.

The main change compared with Figure 2 is the jolt scale of ΔE resulting from the factor 0.65 of E_S in the calculation of E_T. The experimental data are the same, and the same equations are used for the calculated curve, drawn again as a solid line. The change of the relation for the estimation of E_T leads in fact to a much better match of the experimental and calculated data for irreversible EET in the endothermic range. For exothermic EET the same deviations such as those in Figure 2 are observed. The dotted line corresponding to reversible EET again fails to match the experimental data in the slightly exo- and endothermic region in agreement with irreversible EET to quenchers.

4. Conclusion

EET from $O_2(^1\Delta_g)$ to carotenoids occurs not via the electron exchange mechanism according to Dexter. The rate constants k_Δ^Q approach in the exothermic range a limiting maximum value being about 2.6 times smaller than k_d. The magnitude and excess energy dependence of k_Δ^Q can be described using the energy gap law for rate constants of IC of $^{1,3}(T_1{\cdot}^3\Sigma)$ encounter complexes, which was recently derived in the investigation of $T_1(\pi\pi^*)$ state quenching by $O_2(^3\Sigma_g^-)$. The consideration of the appropriate spin-statistical weights and the Boltzmann weighting factor in the case of endothermic energy transfer is sufficient to obtain a quantitative description of $\log(k_\Delta^Q)$ for a large set of literature data. These results demonstrate that EET from $O_2(^1\Delta_g)$ to carotenoids occurs principally by IC of $^1(^1\Delta{\cdot}S_0)$ encounter complexes leading via $^1(T_1{\cdot}^3\Sigma)$ encounter complexes irreversibly to formation of the T_1 excited carotenoid. They furthermore confirm the findings made in the detailed investigations of the quenching of $T_1(\pi\pi^*)$ excited molecules by $O_2(^3\Sigma_g^-)$ and indicate that EET processes to and from O_2 could generally occur via IC of excited complexes.

Acknowledgment. Financial support by the Adolf Messer Stiftung is gratefully acknowledged.

References and Notes

(1) Schweitzer, C.; Schmidt, R. *Chem. Rev.* **2003**, *103*, 1685.
(2) Edge, R.; McGarvey, D. J.; Truscott, T. G. *J. Photochem. Photobiol., B* **1997**, *41*, 189.
(3) Garavelli, M.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 10210.
(4) Bertram, J. S. *Pure Appl. Chem.* **2002**, *74*, 1369.
(5) Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 6233.
(6) Farmilo, A.; Wilkinson, F. *Photochem. Photobiol.* **1973**, *18*, 447.
(7) Foote, C. S.; Chang, Y. C.; Denny, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 5216.
(8) Lambert, C.; Redmond, R. W. *Chem. Phys. Lett.* **1994**, *228*, 495.
(9) Marston, G.; Truscott, T. G.; Wayne, R. P. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4059.
(10) Gorman, A. A.; Hamblett, I.; Lambert, C.; Spencer, B.; Standen, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 8053.
(11) Wessels, J. M.; Rodgers, M. A. J. *J. Phys. Chem.* **1995**, *99*, 17586.
(12) Wilkinson, F.; Ho, W.-T. *Spectrosc. Lett.* **1978**, *11*, 455.
(13) Murasecco-Suardi, P.; Oliveros, E.; Braun, A. M.; Hansen, H.-J. *Helv. Chim. Acta* **1988**, *71*, 1005.
(14) Conn, P. F.; Schalch, W.; Truscott, T. G. *J. Photochem. Photobiol., B* **1991**, *11*, 41.
(15) Oliveros, E.; Braun, A. M.; Aminian-Saghafi, T.; Sliwka, H.-R. *New. J. Chem.* **1995**, *18*, 535.
(16) Devasagayam, T. P. A.; Werner, T.; Ippendorf, H.; Marin, H.-D.; Sies, H. *Photochem. Photobiol.* **1992**, *55*, 511.
(17) Bodesheim, M.; Schütz, M.; Schmidt, R. *Chem. Phys. Lett.* **1994**, *221*, 7.
(18) Schmidt, R.; Shafii, F.; Schweitzer, C.; Abdel-Shafi, A. A.; Wilkinson, F. *J. Phys. Chem. A* **2001**, *105*, 1811.
(19) Schmidt, R.; Shafii, F. *J. Phys. Chem. A* **2001**, *105*, 8871.
(20) Mehrdad, Z.; Noll, A.; Grabner, E.-W.; Schmidt, R. *Photochem. Photobiol. Sci.* **2002**, *1*, 263.
(21) Schweitzer, C.; Mehrdad, Z.; Noll, A.; Grabner, E.-W.; Schmidt, R. *J. Phys. Chem. A* **2003**, *107*, 2192.
(22) Baltschun, D.; Beutner, S.; Briviba, K.; Martin, H.-D.; Paust, J.; Peters, M.; Röver, S.; Sies, H.; Stahl, W.; Steigel, A.; Stenhorst, F. *Liebigs Ann./ Recl.* **1997**, 1887.
(23) Wilkinson, F.; Abdel-Shafi, A. A. *J. Phys. Chem. A* **1999**, *103*, 5425.
(24) Murov, L. S.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Dekker: New York, 1993.
(25) Hirayama, S.; Yasuda, H.; Scully, A. D.; Okamoto, M. *J. Phys. Chem.* **1994**, *98*, 4609.
(26) Borchers, H., Hansen, H., Hellwege, K.-H., Schäfer, K., Schmidt, E., Eds. *Landolt-Börnstein, 6. Auflage, Band II/5a, Transportphänomene I*; Springer-Verlag: Berlin, 1969; p 432.
(27) Schmidt, R.; Bodesheim, M. *Chem. Phys. Lett.* **1993**, *213*, 111.
(28) Shafii, F.; Schmidt, R. *J. Phys. Chem. A* **2001**, *105*, 1805.
(29) Wilkinson, F.; McGarvey, D. J.; Olea, A. F. *J. Phys. Chem.* **1994**, *98*, 3762.
(30) Abdel-Shafi, A. A.; Wilkinson, F. *Phys. Chem. Chem. Phys.* **2002**, *4*, 248.
(31) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(32) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1983.
(33) These values of ΔG_{CET} have been calculated with values of E_{ox} determined in acetonitrile and setting $C = 0$, although the electrostatic interaction energy is definitely positive in the nonpolar CCl_4. Thus, eq 9 holds true only for nonpolar solvents.
(34) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.
(35) Liu, D.; Gao, Y.; Kispert, L. D. *J. Electroanal. Chem.* **2000**, *488*, 140.
(36) The effect of solvent on E_Δ is very small. E_Δ varies only from 94.1 (CF_3CH_2OH) to 93.6 kJ mol^{-1} (CH_5I); see ref 10.
(37) Ford, W. E.; Rihter, B. D.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1989**, *111*, 2362.
(38) Losev, A. P.; Nichiporovich, I. N.; Byteva, I. M.; Drozdov, N. N.; Al Jghgami, I. F. *Chem. Phys. Lett.* **1991**, *181*, 45. (Erratum: *Chem. Phys. Lett.* **1991**, *186*, 586.)
(39) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355.