Chemical Reactivity of Sigma Singlet Oxygen $O_2(^1\Sigma_g^+)$

Marcus Bodesheim and Reinhard Schmidt*

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

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Some of the most reactive $O_2(^1\Delta_g)$ scavengers have been used as substrates to explore the chemical reactivity of $O_2(^1\Sigma_g^+)$ in CCl_4. No chemical deactivation channel could be found. However, an additional physical deactivation by the substrate was observed, which competes with the collision-induced deactivation of $O_2(^1\Sigma_g^+)$ by the substrate and which also leads to the formation of $O_2(^1\Delta_g)$. The rate constant of this additional deactivation of $O_2(^1\Sigma_g^+)$ is very similar to the rate constant of the deactivation of $O_2(^1\Delta_g)$ by the substrate.

Introduction

Singlet oxygen is known to be a very reactive chemical species in photooxygenation reactions.[1−5] However, there are two electronically excited singlet states lying above the $^3\Sigma_g^-$ triplet ground state of O_2, which both could be involved in the singlet oxygen photochemistry. Their excitation energies amount to 94 kJ mol^{-1} for the $^1\Delta_g$ state and 157 kJ mol^{-1} for the $^1\Sigma_g^+$ state.[6] Because of the differences in energy and in electron correlation, it was already early speculated that both singlet state molecules could have a graduated reactivity and even perhaps their own different chemistry.[7−10] The π_g^2 open shell configuration of the O_2 molecule leads to six different electronic substates, one for $^1\Sigma_g^+$, two for $^1\Delta_g$, and three for $^3\Sigma_g^-$. Kasha and Brabham concluded from the analysis of the corresponding wave functions that different mechanisms could be expected for the reactions of O_2 in the three lowest electronic states.[10] The $^1\Sigma_g^+$ state tends to have both antibonding π electrons in plane, so that concerted two-point addition reactions could be visualized. The $^3\Sigma_g^-$ state, in contrast, tends to have each of the π electrons oriented in mutually perpendicular planes. Therefore, intermediates with single-point attachment might be anticipated. The $^1\Delta_g$ state, however, was expected to show both concerted two-point addition and single-point attachment intermediates.[10] Now it is known that the early photochemical investigations for the differentiation of the reactions of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ had been carried out in solvents, in which the lifetime τ_Σ of $O_2(^1\Sigma_g^+)$ is much too short for an efficient competition of a bimolecular chemical reaction with the fast physical deactivation of $O_2(^1\Sigma_g^+)$ by the solvent.[11,12] Such experiments are further complicated by the fact that $O_2(^1\Delta_g)$, which is the product of the physical deactivation of $O_2(^1\Sigma_g^+)$,[13,14] reacts very efficiently with the chosen substrates, due to its several orders of magnitude larger lifetime τ_Δ.

The deactivation of $O_2(^1\Delta_g)$ is strongly forbidden, resulting in very long lifetimes in solution of 3.2 μs (H_2O) $\leq \tau_\Delta \leq$ 0.3 s (perfuorodecalin).[15,16] Thus, delta singlet oxygen is really a metastable species, enabling its well-known chemistry, which consists of the “ene” reaction, the 2 + 2, and the 2 + 4 cycloaddition reactions.[1−4] The collision-induced deactivation $O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-)$ occurs by spin-forbidden electronical to vibrational (e−v) energy transfer to high-frequency stretching modes of terminal bonds of the deactivating solvent molecule.[17] The corresponding rate constant increases roughly exponentially with the fundamental vibrational energy of the deactivating bond.[18,19] The same collisional e−v deactivation mechanism is also operating for sigma singlet oxygen,[20−22] converting $O_2(^1\Sigma_g^+)$ completely to $O_2(^1\Delta_g)$.[14] However, since this deactivation process is spin-allowed and since only 63 kJ mol^{-1} have to be transferred, rapid collisional deactivation takes place, reducing the lifetime τ_Σ of $O_2(^1\Sigma_g^+)$ in solution to very small values, e.g. 130 ps in C_6H_6.[23] A maximum value of τ_Σ was found in CCl_4 with 130 ns.[23,24] Thus, in contrast to $O_2(^1\Delta_g)$, $O_2(^1\Sigma_g^+)$ can only be considered as a metastable species in perchlorinated solvents.

Only after the first time-resolved measurements of $O_2(^1\Sigma_g^+)$ had been published[23] did the development of promising strategies for answering the question of the chemical behavior of sigma singlet oxygen become possible. The first well-founded investigation of the chemical reactivity of $O_2(^1\Sigma_g^+)$ in solution was recently performed by Scurlock et al.[25] The idea was that an efficient reaction of a reactive substrate with $O_2(^1\Sigma_g^+)$ in CCl_4 would prevent its complete transformation to $O_2(^1\Delta_g)$ by collisional deactivation and thus reduce the efficiency of $O_2(^1\Delta_g)$ formation. Furthermore, in this case the experimental rate constants k_Q^Σ of $O_2(^1\Sigma_g^+)$ quenching by the substrate should be larger than the values of k_C^Σ, which can be calculated for the collision-induced deactivation of $O_2(^1\Sigma_g^+)$ by the substrate following the universal e−v energy transfer mechanism.[20−23] $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ produced by photosensitization were monitored directly by observing the respective emissions at 1926 nm ($^1\Sigma_g^+$) and 1275 nm ($^1\Delta_g$).[26,27] The $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ fluorescence could not be detected time resolved. Therefore, the values of k_Q^Σ had to be obtained in Stern−Volmer experiments using the literature value of τ_Σ = 130 ns in CCl_4. Information about the efficiency of $O_2(^1\Delta_g)$ production in the absence or in the presence of added substrates was obtained by extrapolating the comparatively slowly ($\tau_\Delta \geq$ 10 μs) decaying $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ phosphorescence back to time zero. Furan and, in order to reduce the competition by the unavoidable collision-induced deactivation, partially or completely chlorinated dienes or olefins had been chosen as substrates. However, no chemical reaction of $O_2(^1\Sigma_g^+)$ could be detected. The experimental value of k_Q^Σ was for none of the investigated substrates significantly larger than the value of k_C^Σ calculated for the collisional deactivation. The efficiency of $O_2(^1\Delta_g)$ sensitization was in no case reduced, even if the amounts of substrate added were sufficient to quench most of $O_2(^1\Sigma_g^+)$. These results definitely exclude any chemical reaction of $O_2(^1\Sigma_g^+)$ with the investigated substrates, which successfully could compete with the substrate-induced collisional $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ deactivation by the e−v energy transfer.[25]

Like Scurlock et al. we also assume that olefins or dienes could react with $O_2(^1\Sigma_g^+)$ in reactions similar to the “ene” or 2

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+ 4 cycloaddition reactions of $O_2(^1\Delta_g)$. Both types of reactions occur with $O_2(^1\Delta_g)$ most probably via exciplexes with more or less strong charge transfer (CT).[4,28−31] The exciplex decays either by physical deactivation or by a chemical reaction,[28−31] which is assumed to take place via a two-step process (large CT)[30] or in a more concerted way (small CT).[29] Following Kasha and Brabham,[10] concerted reaction paths could be envisaged for the reaction of $O_2(^1\Sigma_g^+)$ with olefins and dienes. Due to its higher energy content, much larger rate constants could be expected than for $O_2(^1\Delta_g)$. Therefore, the possibility that some substrates, which are very reactive $O_2(^1\Delta_g)$ scavengers, might be sufficiently reactive toward $O_2(^1\Sigma_g^+)$ to surpass the physical deactivation by the e−v energy transfer is still not excluded. It was already mentioned by Scurlock et al. that the introduction of chlorine atoms as substituents of the substrates could lead to a reduced reactivity with singlet oxygen[25] because of the concomittant reduction of π-electron density. Furthermore, furan, which presumably was the most reactive substrate toward $O_2(^1\Delta_g)$ in the study of Scurlock et al., deactivates $O_2(^1\Delta_g)$ with a rate constant of only $k_Q^\Delta = 3.6 \times 10^6\ M^{-1}\ s^{-1}$.[32] There are some substrates mentioned in the literature[5] which react much faster with $O_2(^1\Delta_g)$ and which could be better candidates for the discovery or the exclusion of sigma singlet oxygen chemistry. We chose substrates with maximum rate constants of $k_Q^\Delta = 6 \times 10^8\ M^{-1}\ s^{-1}$ in CCl_4. If these compounds, for which k_Q^Δ is not much smaller than the rate constant k_C^Σ of collisional deactivation of $O_2(^1\Sigma_g^+)$, are added in sufficient amounts to quench most of $O_2(^1\Sigma_g^+)$, the lifetime of $O_2(^1\Delta_g)$ is reduced to a few hundred nanoseconds. Thus, an accurate determination of the effect of the substrate on the efficiency of $O_2(^1\Delta_g)$ formation is no more possible by extrapolation of the phosphorescence intensity to time zero. We obtained information about the efficiency of $O_2(^1\Delta_g)$ formation in the presence of a substrate Q by comparing the ratios of the integrated $^1\Delta_g$ emission intensities over the corresponding $^1\Delta_g$ lifetimes of solutions with added substrate Q and with added collisional quencher benzene. Furthermore, we used a different technique, which allowed us to monitor $O_2(^1\Sigma_g^+)$ time resolved by observing the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ emission at 765 nm.[23] Since the $O_2(^1\Sigma_g^+)$ lifetime in CCl_4 is very sensitive to contaminations by the solvent, the time-resolved measurements enable a more accurate determination of the rate constant k_Q^Σ compared with the evaluation of Stern−Volmer experiments basing on $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ emission intensities and the literature value of τ_Σ. For the most reactive compounds we found rate constants k_Q^Σ which significantly surpass the calculated values of k_C^Σ. Thus, our study complements and extends the previous work on the reactivity of sigma singlet oxygen.[25]

Experimental Details

CCl_4 (TET, Janssen, 99+%), and the Aldrich chemicals benzene (BNZ, 99+%), 2,3-dimethyl-2-butene (tetramethylethylene, TME, 99+%), furan (99+%), 2-methylfuran (MEF, 99%), 2-methoxyfuran (MOF, 97%), 2,5-dimethylfuran (DMF, 99%), pyrrole (PYR, 99%), *N*-(2-cyanethyl)pyrrole (NCP, 99+%), *N*-methylpyrrole (NMP, 99%), and phenalenone (PHE, Aldrich, 97%) were purified by column chromatography using Al_2O_3 or silica gel (PHE). Phenazine (PHZ, Fluka > 98%) and 7*H*-benz[*de*]anthracen-7-one (benzanthrone, BAN, Aldrich) were recrystallized from ethanol. Solutions were prepared and filled into sample cells in a glovebox under dry atmosphere. The principal setup for the time-resolved measurements of the $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ phosphorescences has been described.[14,23,33] Briefly, we used as excitation source an excimer laser filled with N_2 (Lambda Physik, EMG 101 E, 337 nm, pulse width 7 ns). Alternatively a dye laser FL 3002, which was pumped by an EMG 200 E excimer laser (both from Lambda Physik) was used for excitation at 400 nm. The sample housing allows the simultaneous observation of two emissions in T arrangement. In this way, the formation and decay of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ can be followed simultaneously by their corresponding phosphorescence traces at 765 nm (R1464 photomultiplier, Hamamatsu) and 1276 (liquid N_2 cooled germanium diode EO 817P, North Coast). The emissions were isolated by suited interference filters. The purified quenchers did not absorb at 337 nm with the exception of MOF, which was excited at 400 nm. The absorbances of the sensitizers amounted to about 1 per cm at the excitation wavelengths and were kept constant in the quenching experiments. The time-resolved experiments allowed control of the triplet state lifetime τ_T of the sensitizers. τ_T was not affected by the addition of the quenchers used. All emission experiments were done with air-saturated solutions at room temperature varying the laser pulse energy. Only energy-independent results are reported. Photochemical experiments for the determination of the ratio k_R^Δ/k_Q^Δ of the rate constants of chemical and overall deactivation of $O_2(^1\Delta_g)$ by NMP were performed under continuous irradiation of the sensitizers PHE or PHZ in a setup described already earlier.[34] The oxygen consumption rate was measured in comparison to the scavenger TME, which is known to deactivate $O_2(^1\Delta_g)$ exclusively by chemical reaction.[29,35]

Results and Discussion

$^1\Sigma \equiv O_2(^1\Sigma_g^+)$, $^1\Delta \equiv O_2(^1\Delta_g)$, and $^3\Sigma \equiv O_2(^3\Sigma_g^-)$ are formed with corresponding efficiencies a, b, and $1 - a - b$ in the photosensitization of O_2 by the triplet state (T_1) sensitizers PHE, PHZ and BAN in air-saturated TET.[36] The radiative deactivation of T_1, $^1\Sigma$, and $^1\Delta$ is negligible.[14,23,33] The following equations describe the principal deactivation paths of the different excited species.

$$T_1 + {}^3\Sigma \rightarrow S_0 + {}^1\Sigma \qquad ak_O^T \tag{1}$$

$$T_1 + {}^3\Sigma \rightarrow S_0 + {}^1\Delta \qquad bk_O^T \tag{2}$$

$$T_1 + {}^3\Sigma \rightarrow S_0 + {}^3\Sigma \qquad (1 - a - b)k_O^T \tag{3}$$

$$^1\Sigma + M \rightarrow M + {}^1\Delta \qquad k_M^\Sigma \tag{4}$$

$$^1\Sigma + Q \rightarrow Q + {}^1\Delta \qquad k_C^\Sigma \tag{5}$$

$$^1\Sigma + Q \rightarrow P_\Sigma \qquad k_R^\Sigma \tag{6}$$

$$^1\Delta + M \rightarrow M + {}^3\Sigma \qquad k_M^\Delta \tag{7}$$

$$^1\Delta + Q \rightarrow Q + {}^3\Sigma \qquad k_P^\Delta \tag{8}$$

$$^1\Delta + Q \rightarrow P_\Delta \qquad k_R^\Delta \tag{9}$$

S_0, M, and Q represent the ground state sensitizer, solvent molecules and the added substrates listed in Table 1. P_Σ and P_Δ are the products of reactions of $^1\Sigma$ and $^1\Delta$ with Q. The superscripts T, Σ, and Δ of the rate constants k denote the excited state, which is quenched. The subscripts O and M refer to quencher O_2 and solvent M. The subscripts P and R indicate the physical and the reactive deactivation by the added substrate Q. Thus, $k_Q^\Delta = k_P^\Delta + k_R^\Delta$ holds true. k_C^Σ is the rate constant of collisional deactivation of $O_2(^1\Sigma_g^+)$ by Q following the e−v energy transfer. We obtain as lifetimes of T_1, $^1\Sigma$, and $^1\Delta$:

TABLE 1: Experimental Rate Constants k_Q^{Δ} and k_Q^{Σ} of Quenching of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ by Different Substrates Q, and Rate Constants k_C^{Σ} of Collisional Quenching of $O_2(^1\Sigma_g^+)$ Calculated According to the e−v Energy Transfer Mechanism[a]

Q	k_Q^{Δ}	k_Q^{Σ}	k_C^{Σ}	$k_C^{\Sigma} + k_Q^{\Delta}$
TME[b]	0.15 ± 0.03	11 ± 1.7	12 ± 2	12.2 ± 2
MEF[b]	0.6 ± 0.1	7.8 ± 1.5	6 ± 1	6.6 ± 1
MOF[b]	1.5 ± 0.1	6.3 ± 1.1	6 ± 1	7.5 ± 1
DMF[b]	3.2 ± 0.4	9.8 ± 1.5	8 ± 1.5	11.2 ± 1.5
PYR[d]	1.2 ± 0.1	12.1 ± 2.9	9 ± 1.5	10.2 ± 1.5
NCP[c]	3.1 ± 0.7	11.6 ± 2.7	8 ± 1.5	11.1 ± 1.5
NMP[d]	6.0 ± 0.5	13.5 ± 1.4	7 ± 1	13.0 ± 1

[a] All rate constants are in units of 10^8 M^{-1} s^{-1}. [b] Sensitizer PHE. [c] Sensitizers PHE and PHZ. [d] Sensitizers PHE, PHZ, and BAN.

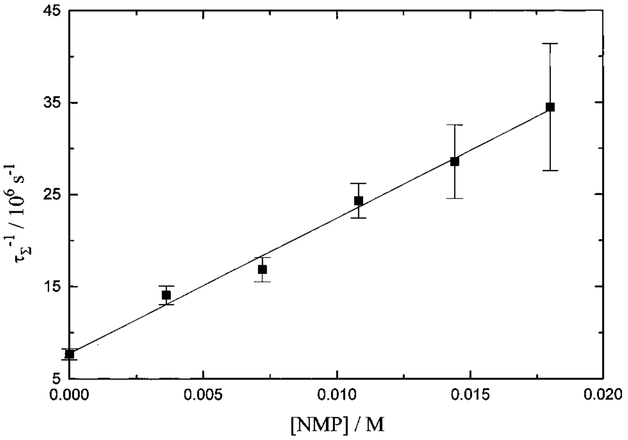

Figure 1. Correlation of $1/\tau_\Sigma$ with [NMP] in TET. $k_Q^{\Sigma} = (14.7 \pm 1.0) \times 10^8$ M^{-1} s^{-1}.

$\tau_T = (k_O^T[O_2])^{-1}$, $\tau_\Sigma = (k_M^{\Sigma} + (k_C^{\Sigma} + k_R^{\Sigma})[Q])^{-1}$ and $\tau_\Delta = (k_M^{\Delta} + (k_P^{\Delta} + k_R^{\Delta})[Q])^{-1}$.

Equation 10 describes the rise and decay of $[^1\Sigma]_t$. The

$$[^1\Sigma]_t = [T_1]_0 a\tau_\Sigma/(\tau_\Sigma - \tau_T)\{\exp(-t/\tau_\Sigma) - \exp(-t/\tau_T)\} \quad (10)$$

emission $I_{765}(t)$ observed at 765 nm consists of a very intense, fast-decaying background luminescence $L(t)$ followed by the $^1\Sigma$ phosphorescence.[14,23] If 7 vol % BNZ are added to the solution, the $^1\Sigma$ emission is quenched completely, whereas $L(t)$ remains unchanged. Therefore, the difference signal $\Delta I_{765}(t) = I_{765}(t) - L(t)$ is directly proportional to $[^1\Sigma]_t$. Lifetimes τ_T and τ_Σ are obtained by nonlinear least-squares fitting of convolutions of the apparatus function (photomultiplier response to the laser pulse) with eq 10 to the experimental curves $\Delta I_{765}(t)$.[23] Variation of [Q] influenced τ_Σ but not τ_T, which demonstrates that the substrate Q does not deactivate the sensitizer triplet. Plots of $1/\tau_\Sigma$ versus [Q] are linear as is exemplarily demonstrated in Figure 1 for the substrate NMP. The slope of the linear least-squares fit is the overall quenching constant $k_Q^{\Sigma} = k_C^{\Sigma} + k_R^{\Sigma}$. Values of k_Q^{Σ} obtained for the different substrates are listed in Table 1.

The rise and decay of $[^1\Delta]_t$ follows eq 11 with $A = [T_1]_0\tau_\Delta/$

$$[^1\Delta]_t = A\{\exp(-t/\tau_\Delta) - \exp(-t/\tau_T)\} + B\{\exp(-t/\tau_\Sigma) - \exp(-t/\tau_T)\} \quad (11)$$

$(\tau_\Delta - \tau_T)\{b + ac\tau_\Delta/(\tau_\Delta - \tau_\Sigma)\}$, $B = [T_1]_0 ac\tau_\Sigma\tau_\Delta/(\tau_\Delta - \tau_\Sigma)/(\tau_T - \tau_\Sigma)$, and c being the efficiency of $^1\Delta$ formation in the $^1\Sigma$ deactivation. If $^1\Sigma$ is only quenched by collisional deactivation according to the e−v mechanism as it is the case for TET and BNZ, then $c = 1$.[14] Equation 11 is too complex to be used in the nonlinear least-squares fitting of convolutions with the apparatus function (Ge diode response to the laser pulse) to the experimental $^1\Delta$ phosphorescence curves $I_{1275}(t)$. However, if 7 vol % BNZ are added to the solution, $^1\Sigma$ is very rapidly quenched by collisional deactivation and $c = 1$, $\tau_\Sigma = 1.8$ ns $\ll \tau_\Delta$, τ_T results, leading to eq 12. Then, of course, the lifetime of $^1\Delta$ is reduced to about 350 μs already in the absence of substrate Q.

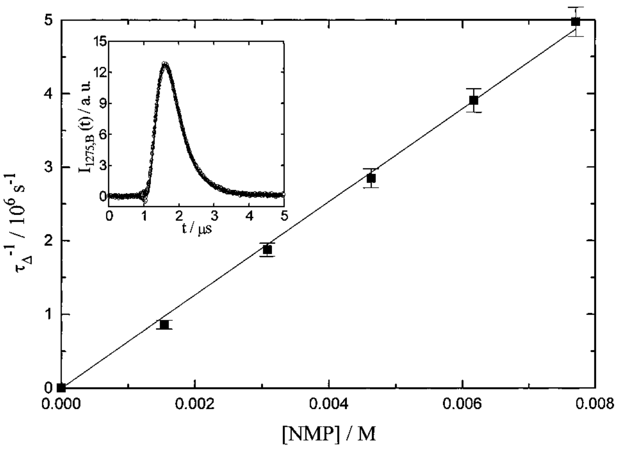

Figure 2. Correlation of $1/\tau_\Delta$ with [NMP] in TET + 7 vol % BNZ. $k_Q^{\Delta} = (6.3 \pm 0.2) \times 10^8$ M^{-1} s^{-1}. Inset: Rise and decay of the $O_2(^1\Delta_g)$ phosphorescence at 1275 nm. Open circles are experimental data, curve represents convolution of apparatus function with eq 12, $\tau_T = 245$ ns and $\tau_\Delta = 353$ ns. Sensitizer PHZ, [NMP] = 0.004 63 M.

$$[^1\Delta]_{t,B} = [T_1]_0(b + a)\tau_\Delta/(\tau_\Delta - \tau_T)\{\exp(-t/\tau_\Delta) - \exp(-t/\tau_T)\} \quad (12)$$

Equation 12 is used to fit the $^1\Delta$ phosphorescence $I_{1275,B}(t)$ in mixtures of TET and 7 vol % BNZ by convolution techniques. τ_Δ and τ_T are obtained. If the substrate Q is present in the solvent mixture in such high concentrations that deactivation of $^1\Delta$ occurs only by Q ($\tau_\Delta \approx 1$ μs), then τ_Δ is reciprocally related with [Q]. The value of τ_T was not affected by the substrates. Figure 2 demonstrates exemplarily for the substrate NMP the linear correlation of $1/\tau_\Delta$ with [Q]. The slope of the linear least-squares fit is the overall quenching constant $k_Q^{\Delta} = k_P^{\Delta} + k_R^{\Delta}$. Values of k_Q^{Δ} obtained for the different substrates are collected in Table 1.

Our values of k_Q^{Δ} are in line with literature data. k_Q^{Δ} depends only moderately on the solvent polarity for TME, which is a purely chemical quencher of $O_2(^1\Delta_g)$.[35] For example, k_Q^{Δ} amounts (in units of 10^8 M^{-1} s^{-1}) to 0.64 (benzonitrile),[37] 0.42 (CH_2Cl_2),[37] 0.32, 0.36 (toluene),[37,38] 0.22 (CS_2),[39] and 0.092 (*n*-hexane).[37] The furan derivatives deactivate $O_2(^1\Delta_g)$ also only chemically.[29] Values of 1.0 (CH_3OH)[29] and 0.62 (CH_2Cl_2)[40] have been reported for MEF, 1.6 (CH_3OH),[29] and 1.2 (CH_2Cl_2)[40] for MOF, 1.8 (CH_3OH),[29] 1.6 (CH_2Cl_2),[40] and 6.3 (toluene)[41] for DMF. Less data are available for pyrrole derivatives: 1.7 (toluene)[42] for PYR, for which we obtained 2.4 (toluene) and 4.7 (CH_3CN), and 3.7 (toluene)[42] and 10 (CCl_4)[43] for NMP.

Rate constants of collisional deactivation of singlet oxygen are composed additively from incremental rate constants k_{XY} of deactivation by terminal bonds X−Y. This has been shown to hold true for $O_2(^1\Delta_g)$[17−20] as well as for $O_2(^1\Sigma_g^+)$.[20−23] From our data on the collisional deactivation of $O_2(^1\Sigma_g^+)$ we calculate $k_{CH}^{\Sigma} = (1.0 \pm 0.2) \times 10^{8}$[23] and $k_{NH}^{\Sigma} = (5 \pm 1.5) \times 10^8$ M^{-1} s^{-1}.[44] Both numbers can be taken to calculate the rate constants k_C^{Σ} of collisional deactivation of $O_2(^1\Sigma_g^+)$ according to the e−v energy transfer for the substrates used. These data are given for means of comparison in Table 1. For TME we find k_Q^{Σ}

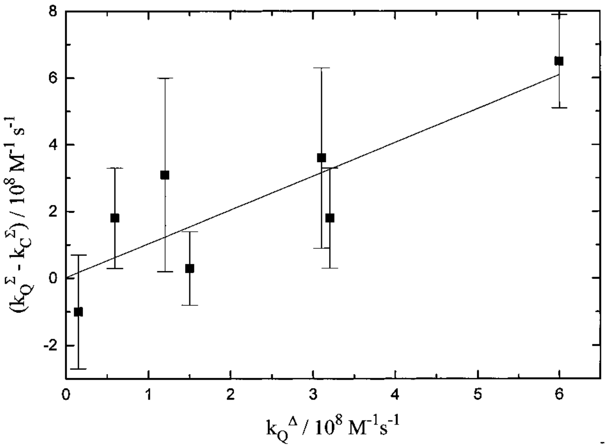

Figure 3. Correlation of $k_Q^\Sigma - k_C^\Sigma$ with k_Q^Δ data of Table 1. The straight line represents the linear least-squares fit with slope 1.0 ± 0.3 and intercept 0.0 ± 1.5.

slightly smaller than k_C^Σ, but considering the error limits $k_Q^\Sigma = k_C^\Sigma$. Obviously, k_R^Σ must be much smaller than k_C^Σ. Therefore, the photooxygenation of TME takes place only via $O_2(^1\Delta_g)$. The possibility of the reaction of $O_2(^1\Sigma_g^+)$ with TME and 1,1-dimethyl-2,2-dimethoxyethylene was already earlier investigated in gas phase experiments by Hammond.[45] $O_2(^1\Sigma_g^+)$ was produced in mixtures of O_2 and olefin by resonant absorption $^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$. His findings allowed only two alternative conclusions: (1) The olefins react with both $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ under formation of identical products or (2) $O_2(^1\Sigma_g^+)$ is collisionally deactivated to $O_2(^1\Delta_g)$, before the reaction of olefin and $O_2(^1\Delta_g)$ takes place. Our results confirm Hammond's conclusion (2). Since TME and 1,1-dimethyl-2,2-dimethoxyethylene belong to the most reactive olefins, it appears that $O_2(^1\Sigma_g^+)$ is chemically not reactive with olefins.

For MEF, MOF, and DMF, which are more reactive $O_2(^1\Delta_g)$ scavengers, k_Q^Σ is larger than k_C^Σ, but the deviation is only about as large as the experimental uncertainty. However, for PYR, NCP, and NMP k_Q^Σ is distinctly larger than k_C^Σ. If this finding would have been made only for one of the pyrroles, we would deny the significance of the difference, which actually is only a little bit larger than the error limits. But as we find a distinct difference for all three pyrroles, and since there is a trend for increasing difference $k_Q^\Sigma - k_C^\Sigma$ with increasing value of k_Q^Δ, which is illustrated by the correlation of Figure 3, we take the inequality $k_Q^\Sigma > k_C^\Sigma$ to be true.

Thus, for the first time besides the ubiquitous collision-induced deactivation an additional channel for the deactivation of $O_2(^1\Sigma_g^+)$ is observed, which could well be a chemical reaction with the substrates. Table 1 compares the sums $k_C^\Sigma + k_Q^\Delta$ with the experimental rate constants k_Q^Σ. A good agreement between these values has to be noted. This finding demonstrates that $O_2(^1\Sigma_g^+)$ reacts on no account faster with the investigated substrates than $O_2(^1\Delta_g)$. This is a surprising result, since one would expect a much higher reactivity of $O_2(^1\Sigma_g^+)$ because of its by 63 kJ mol^{-1} larger excitation energy. The correlation of Figure 3 of $k_Q^\Sigma - k_C^\Sigma$ versus k_Q^Δ with slope 1.0 ± 0.3 shows that the additional deactivation of $O_2(^1\Sigma_g^+)$ by Q occurs with approximately the same rate constant as the deactivation of $O_2(^1\Delta_g)$ by Q. This very interesting result will be discussed below.

TABLE 2: Comparison of the Substrate Concentration Dependence of Experimental and Calculated Values of $R = (b + ac_Q)/(b + a)$[a]

[PYR], M	R_{exp}	R_{calc}	[NMP], M	R_{exp}	R_{calc}
0	1.00 ± 0.05	1.00	0	1.00 ± 0.05	1.00
0.0037	1.12 ± 0.09	0.92	0.0024	1.05 ± 0.08	0.88
0.0074	1.00 ± 0.06	0.88	0.0048	1.04 ± 0.08	0.81
0.0111	0.96 ± 0.06	0.86	0.0072	1.05 ± 0.08	0.77
0.0148	1.03 ± 0.13	0.85	0.0096	1.06 ± 0.13	0.74
0.0185	1.01 ± 0.15	0.84	0.0120	1.02 ± 0.18	0.72

[a] Details are described in the text.

If the additional deactivation channel for $O_2(^1\Sigma_g^+)$ is actually due to a chemical reaction with the substrate Q, the efficiency of the photosensitized $O_2(^1\Delta_g)$ formation must be reduced in the presence of Q. Integration of $[^1\Delta]_t$ (eq 11) in the limits $t = 0$ to ∞ leads to the simple eq 13, where the sum $b + ac$ represents the overall efficiency of indirectly (ac) via $O_2(^1\Sigma_g^+)$ and directly (b) formed $O_2(^1\Delta_g)$ in the sensitization of O_2 by T_1. Equation 13 allows the investigation, on whether a substrate

$$\mathrm{INT}_\Delta = [T_1]_0 \tau_\Delta (b + ac) \tag{13}$$

Q reduces the efficiency of $^1\Delta$ formation in $^1\Sigma$ deactivation. In the absence of BNZ and in the presence of a $^1\Sigma$ deactivating substrate Q the efficiency of $^1\Delta$ formation in $^1\Sigma$ deactivation is c_Q. If Q deactivates $^1\Sigma$ also by chemical reaction, c_Q becomes smaller than unity. The ratio of the integrated $^1\Delta$ phosphorescence intensity INT_{1275} over the respective $^1\Delta$ lifetime is then given by eq 14, where f is a constant which is directly proportional to the rate constant of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ emission. If

$$(\mathrm{INT}_{1275}/\tau_\Delta)_Q = f[T_1]_0(b + ac_Q) \tag{14}$$

no substrate Q but 7 vol % BNZ are present in the TET solution of the sensitizer $c = 1$, and the respective ratio $(\mathrm{INT}_{1275}/\tau_\Delta)_B$ is given by eq 15 with constant f'.

$$(\mathrm{INT}_{1275}/\tau_\Delta)_B = f'[T_1]_0(b + a) \tag{15}$$

In these experiments we have to consider that the radiative rate constant of the $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ emission depends on the solvent.[46] The relative rate constant of emission amounts to 0.73 s^{-1} in TET related to 1 s^{-1} in BNZ.[33] It was shown by us that the emission is a bimolecular collision-induced process.[33] Therefore, we calculate the relative values of the second-order rate constants of phosphorescence of 0.071 M^{-1} s^{-1} (TET) and 0.089 M^{-1} s^{-1} (BNZ) and from the molarities of TET and BNZ in the mixture of 7 vol % BNZ in TET $f' = 1.025f$. Experiments were performed with BAN, which sensitizes $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ with efficiencies of $a = 0.85$ and $b = 0.15$, respectively.[36] NMP and PYR were the substrates Q. We determined the experimental energy normalized ratios $R_{exp} = 1.025(\mathrm{INT}_{1275}/\tau_\Delta)_Q/(\mathrm{INT}_{1275}/\tau_\Delta)_B = (b + ac_Q)/(b + a)$, which are listed in Table 2.

Efficiencies c_Q can be estimated by eq 16, $k_M^\Sigma = (130\ \mathrm{ns})^{-1}$,

$$c_Q = (k_M^\Sigma + k_C^\Sigma[Q])/(k_M^\Sigma + k_Q^\Sigma[Q]) \tag{16}$$

and the data of k_Q^Σ and k_C^Σ. These values can then be used to calculate ratios $R_{calc} = (b + ac_Q)/(b + a)$, which are compared in Table 2 with values of R_{exp}. R represents the ratio of the overall efficiency of $O_2(^1\Delta_g)$ formation in the presence of a substrate in concentration [Q] over the overall efficiency of $O_2(^1\Delta_g)$ formation under conditions of pure collision induced deactivation of $O_2(^1\Sigma_g^+)$. For PYR a decrease of R_{calc} by 16% is expected at the maximum substrate concentration if Q would react with $O_2(^1\Sigma_g^+)$ with rate constant $k_Q^\Sigma - k_C^\Sigma$. But we observe no significant decrease of R_{exp} with increasing [PYR]. The data scatter around a mean value of 1.00, if the deviating value $R_{exp} = 1.12$ at [PYR] = 0.037 M is neglected. The results are even more definite for NMP, where a decrease of R_{calc} by 28% is expected but no decrease of R_{exp} is found.

These findings show that the additional $O_2(^1\Sigma_g^+)$ deactivation channel leads to the formation of $O_2(^1\Delta_g)$. There is neither a particular chemical reaction of $O_2(^1\Sigma_g^+)$ nor a physical process which bypasses $O_2(^1\Delta_g)$ in the additional deactivation of $O_2(^1\Sigma_g^+)$. The net effect of the additional physical deactivation process is quantitative conversion $^1\Sigma \rightarrow {}^1\Delta$. Thus eq 6 of the reaction scheme has to be replaced by eq 6a with rate constant

$$^1\Sigma + Q \rightarrow Q + {}^1\Delta \qquad k_P^{\Sigma} \tag{6a}$$

$k_P^{\Sigma} = k_Q^{\Sigma} - k_C^{\Sigma}$. The observation $k_P^{\Sigma} \approx k_Q^{\Delta}$ (compare Figure 3) lets us suspect that the deactivation process 6a is intimately related with the deactivation of $O_2(^1\Delta_g)$ via the processes 8 and 9. The reaction of $O_2(^1\Delta_g)$ with cyclic dienes occurs as $2 + 4$ cycloaddition forming endoperoxides in the primary step.[1−4] In temperature-dependent investigations (olefins, enol ethers, furan derivatives, indoles), it was found that the reaction requires practically no activation enthalpy.[38,39,41,47] Therefore, it is assumed that an exciplex with some CT is formed as intermediate.[4,28,38] Generally, for most substrates a competition between physical—possibly CT mediated[48,49]—and chemical deactivation of $O_2(^1\Delta_g)$ is observed, whereby already small sterical variations of the substrate can be sufficient to change the balance between the deactivation processes drastically.[50] There is strong evidence that the competing processes occur via the same intermediate, which is formed in the rate-determining step,[28,30,31] and which collapses either under formation of an endoperoxide or in the physical deactivation step. Whereas it is known that the deactivation of $O_2(^1\Delta_g)$ by MEF, MOF, and DMF occurs completely by chemical reaction, i.e., $k_R^{\Delta} = k_Q^{\Delta}$,[29] no respective data have been found for the pyrrole derivatives, which are also known to react with $O_2(^1\Delta_g)$.[2] We therefore determined under identical sensitization conditions the O_2-consumption rate by NMP in comparison to the scavenger TME. The experiments resulted in $k_R^{\Delta} \leq 0.1 k_Q^{\Delta}$, i.e., $O_2(^1\Delta_g)$ is deactivated by NMP principally physically, probably by a CT mediated process. However, since the chemical reactions of pyrroles with $O_2(^1\Delta_g)$ proceed also via endoperoxides,[2] similar intermediates as for the furan derivatives can be assumed. A transition state in which the oxygen atoms lie above the carbon atoms in the 2- and 5-positions of the heterocycle seems reasonable.

Since $\Delta H^{\ddagger} \approx 0$, the activation entropy $\Delta S^{\ddagger}$ determines the value of k_Q^{Δ} for the chemical and/or physical deactivation of $O_2(^1\Delta_g)$. $\Delta H^{\ddagger} \approx 0$ can also be expected for the deactivation of $O_2(^1\Sigma_g^+)$, because of its larger excitation energy. If one accepts this assumption, the finding $k_P^{\Sigma} \approx k_Q^{\Delta}$ demonstrates that the $O_2(^1\Sigma_g^+)$ deactivation and the deactivation of $O_2(^1\Delta_g)$ require practically the same activation entropy, indicating the same transition states. Therefore, we propose that the deactivation of $O_2(^1\Sigma_g^+)$ by process 6a proceeds via the transition state for the deactivation of $O_2(^1\Delta_g)$ by the heterocyclic diene: As soon as the new bonds between oxygen and carbon atoms begin to form in the approach to the transition state, the door to a large heat bath is opened, in which the excess excitation energy of $O_2(^1\Sigma_g^+)$ versus $O_2(^1\Delta_g)$ is instantaneously released as heat, leading to dissociation into $O_2(^1\Delta_g)$ and substrate. 63 kJ mol^{-1} have to be distributed. Assuming that the excess energy is completely transferred to the heat bath of the substrate, we estimate from the molar heat capacity of $C_p = 128$ J mol^{-1} K^{-1} of PYR[51] a maximum value for the instantaneous jump of the internal temperature of PYR of about 500 K. If the energy is distributed in the way that both PYR and $O_2(^1\Delta_g)$ ($C_p = 29$ J mol^{-1} K^{-1})[51] take the same temperature, then the temperature jump still amounts to about 400 K, which certainly is sufficient to explain the observed dissociation into $O_2(^1\Delta_g)$ and substrate subsequent to deactivation. Furthermore, dissociation is preferred to reaction of $O_2(^1\Delta_g)$ and substrate as the values of k_Q^{Δ} are at least about 2 orders of magnitude smaller than the rate constant of diffusion, indicating a very small reaction probability of $O_2(^1\Delta_g)$ and substrate per encounter. The deactivation process 6a is electronically allowed like the collision-induced $O_2(^1\Sigma_g^+) \rightarrow O_2(^1\Delta_g)$ transition, for which the electronic factor is near by unity.[22] In addition, the coupling between the heat bath of the substrate and $O_2(^1\Sigma_g^+)$ should become much stronger during the approach to the transition state than in a simple collision, where no bonds are formed. The proposed coupling of $O_2(^1\Sigma_g^+)$ with the heat bath of the substrate in the region of the transition state can, however, not induce the spin-forbidden deactivation process $^1\Sigma \rightarrow {}^3\Sigma$ because of the corresponding poor electronic factor. For example, the ratio of the electronic factors of the collision-induced deactivation processes $^1\Delta \rightarrow {}^3\Sigma$ and $^1\Sigma \rightarrow {}^1\Delta$ was determined to be only 6×10^{-5}.[20,22]

The lack of formation of an endoperoxide PO by a chemical reaction of $O_2(^1\Sigma_g^+)$ with Q can be understood by a consideration of the corresponding energy balance. POs of aromatic compounds split thermally with activation enthalpies between 125 and 140 kJ mol^{-1} into $O_2(^1\Delta_g)$ and aromatic substrate.[52−56] Assuming $\Delta H^{\ddagger}$ for the reverse reaction to be close to zero, results in an estimate for the reaction enthalpy of PO formation from ground state O_2 and aromatic compound of $\Delta H \approx -30$ to -45 kJ mol^{-1}. Therefore, the one-step formation of PO from Q and $O_2(^1\Sigma_g^+)$ would release an amount of energy of roughly 190 kJ mol^{-1}, which is much larger than the activation enthalpy of PO cleavage and would provoke dissociation into $O_2(^1\Delta_g)$ and Q. Actually, it was already shown for the PO of 2,5-diphenylfuran that the thermal cleavage of the PO yields furan and $O_2(^1\Delta_g)$.[57,58] Thus, the immediate dissociation after deactivation $^1\Sigma \rightarrow {}^1\Delta$ in the region of the transition state of PO formation appears to be reasonable.

Conclusions

Our investigations on the chemical reactivity $O_2(^1\Sigma_g^+)$ were focused on some of the most reactive $O_2(^1\Delta_g)$ scavengers. No chemical deactivation channel of $O_2(^1\Sigma_g^+)$ could be detected. However, we observed an additional physical deactivation process, which competes with the general collision-induced deactivation of $O_2(^1\Sigma_g^+)$ by the e−v energy transfer and which also leads to the formation of $O_2(^1\Delta_g)$. Since k_P^{Σ} is very similar to k_Q^{Δ}, it is assumed that $O_2(^1\Sigma_g^+)$ walks on the reaction path of $O_2(^1\Delta_g)$ approaching the same transition state, at least for the furan and pyrrole derivatives. It is assumed that deactivation $^1\Sigma \rightarrow {}^1\Delta$ occurs in the region of the transition state of PO formation. As soon as the new bonds between oxygen and carbon atoms begin to form, the door to a large heat bath is opened, in which the excess excitation energy of $O_2(^1\Sigma_g^+)$ versus $O_2(^1\Delta_g)$ is instantaneously released as heat leading to dissociation into $O_2(^1\Delta_g)$ and substrate. Obviously, the chemistry of $O_2(^1\Sigma_g^+)$ is prevented by its lability with respect to spin-allowed deactivation. The approach to any transition state would lead with beginning bond formation to an efficient coupling of the heat bath of the substrate to $O_2(^1\Sigma_g^+)$ inducing instantaneously deactivation and formation of $O_2(^1\Delta_g)$. Therefore, we conclude that $O_2(^1\Sigma_g^+)$ is generally chemically not reactive.

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