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Determination of Rate Constants of Formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ in the Quenching of Triplet States by O_2 for Compounds with Incomplete Intersystem Crossing†

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The separate determination of the rate constants of the competitive formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ in the deactivation of the triplet state by O_2 of sensitizers with incomplete intersystem crossing is exemplarily demonstrated with naphthalene. The method is based on triplet−triplet energy transfer in CCl_4 from a primary sensitizer to the sensitizer of interest. Because of the very fast quenching of $O_2(^1\Sigma_g^+)$ by hydrocarbons, the conditions of these experiments are rather stringent. All the different energy transfer steps involved have to be quantitatively determined. This is done by examining the phosphorescence of the primary sensitizer as well as the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$, $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$, and $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ emissions of O_2 in air-saturated CCl_4.

Introduction

Both excited $^1\Sigma_g^+$ and $^1\Delta_g$ singlet states of oxygen can be formed besides the $^3\Sigma_g^-$ triplet ground state in the quenching of triplet states T_1 by O_2. Quantum yields of sensitization of $O_2(^1\Delta_g)$ have been measured for hundreds of sensitizers because of the outstanding importance of $O_2(^1\Delta_g)$ as highly reactive chemical species.[1,2] Despite the large number of data and numerous efforts, no clear relation was found between the efficiency S_Δ of $O_2(^1\Delta_g)$ sensitization in the quenching of the T_1 state by O_2 and the molecular parameters of the sensitizer such as its triplet energy E_T or its oxidation potential E_{ox}.[3−8] One of the main reasons for that unsatisfying situation was the missing differentiation between $O_2(^1\Delta_g)$ being directly formed and $O_2(^1\Delta_g)$ indirectly formed via the very short-lived upper excited $O_2(^1\Sigma_g^+)$, which was not possible in these experiments.

Deeper insight into the processes competing in the deactivation of T_1 by O_2 could only be gained when we developed a method for the separate determination of the rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ formation by sensitizers with complete intersystem crossing (isc).[9] We determined these rate constants for 13 triplet sensitizers and found that they depend in a common way on the excess energy ΔE of the respective deactivation process for sensitizers with $E_T \lesssim 220$ kJ mol^{-1}.[10] Through this, we discovered for the first time a quantitative relation between $S_\Delta = (k_T^{1\Sigma} + k_T^{1\Delta})/(k_T^{1\Sigma} + k_T^{1\Delta} + k_T^{3\Sigma})$ and E_T.

For sensitizers with larger triplet energies, charge-transfer effects accelerate the formation of singlet oxygen and ground-state oxygen in the deactivation of triplet states by O_2.[4−8] For deeper insight to be gained in the combined effects of E_{ox} and E_T on $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$, the knowledge of these rate constants is very important for a larger variety of triplet sensitizers with $E_T \gtrsim 220$ kJ mol^{-1}. However, most of these high energy sensitizers have only incomplete isc,[11] which complicates such measurements, since (1) the sensitization of singlet oxygen could also occur via the lowest excited singlet state S_1 and since (2) the measurement of the very weak $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ and $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ emissions of O_2 can be severely disturbed by the relatively strong sensitizer fluorescence. The indirect population of T_1 by triplet−triplet (TT) energy transfer from the primary sensitizer (S1) benzophenone with isc quantum yield $Q_T = 1$ has been shown to be a very useful method to circumvent these problems if only $O_2(^3\Sigma_g^-)$ and the entirely formed $O_2(^1\Delta_g)$ are of interest.[4,6] For diffusion-controlled TT energy transfer, concentrations of the secondary sensitizer (S2) of interest of 0.1 M are sufficient for complete indirect excitation of the T_1 state of S2.

However, the separate determination of $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ is not possible under these conditions. $O_2(^1\Sigma_g^+)$ is very rapidly and completely deactivated to $O_2(^1\Delta_g)$ by spin-allowed electronical to vibrational (e−v) energy transfer to the terminal bonds of colliders.[9,12,13] Since the rate constant k_Σ of $O_2(^1\Sigma_g^+)$ deactivation exponentially increases with the energy of the stretching vibration of the deactivating bond, molecules with O−H, N−H, and C−H bonds belong to the strongest quenchers of $O_2(^1\Sigma_g^+)$, whereas the weakest quenchers are perchlorinated compounds.[12] Actually, the lifetime of $O_2(^1\Sigma_g^+)$ is relatively long in liquid CCl_4, where τ_Σ amounts to about 130 ns.[13−17] Since one aromatic C−H bond deactivates $O_2(^1\Sigma_g^+)$ with $k_\Sigma \approx 1.1 \times 10^8$ M^{-1} s^{-1}, a secondary sensitizer like naphthalene will quench $O_2(^1\Sigma_g^+)$ with $k_\Sigma^Q \approx 9 \times 10^8$ M^{-1} s^{-1}.[13] Consequently, the presence of 0.1 M naphthalene will reduce τ_Σ in CCl_4 to about 10 ns, which presently is too low for time-resolved measurements of $O_2(^1\Sigma_g^+)$.[13,18] Thus, the concentration of S2 has to be significantly reduced. The quenching of T_1(S1) by O_2 competes with TT energy transfer to S2 in air-saturated solvents. Consequently, the benefits with respect to τ_Σ of the necessary decrease of [S2] will partially be compensated by the disatvantage caused by the increasing amount of sensitization of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ by T_1(S1), which adds to the actually interesting sensitization of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ by T_1(S2). In the present paper, we demonstrate by a comparative investigation of the sensitizer combination benzophenone (S1) and naphthalene (S2) with the reference

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† Dedicated to Professor Dr. H.-D. Brauer on the occasion of his retirement.

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sensitizer phenalenone that the above-mentioned indirect population of the T_1 state of an interesting sensitizer with incomplete isc still can be used to separately determine the rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$, and $k_T^{3\Sigma}$ in CCl_4 if the different energy transfer steps involved have quantitatively been determined.

Experimental Details

CCl_4 (Acros, 99+%) was dried by column chromatography (Al_2O_3). Phenalenone (PHE, Aldrich, 97%) was purified by column chromatography (CH_2Cl_2/silica gel). Benzophenone (BPH, Fluka, 99+%) and naphthalene (NAPH, Fluka, 98+%) were additionally purified by crystallization from ethanol and pentane, respectively. Erythrosin B (Aldrich, 95%) and benzene (BNZ, Aldrich, 99+%) were used as supplied. The solutions were prepared and filled into sample cells in a glovebox under dry atmosphere to avoid the uptake of humidity in the investigation of $O_2(^1\Sigma_g^+)$. These particular precautions are not necessary in the investigation of T_1(BPH) via its phosphorescence. The experimental setup allows the simultaneous time-resolved measurement of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ via the $^1\Sigma_g^+ \rightarrow {}^3\Sigma_g^-$ (765 nm) and $^1\Delta_g \rightarrow {}^3\Sigma_g^-$ (1275 nm) phosphorescences and the integral detection of $O_2(^1\Sigma_g^+)$ via the $^1\Sigma_g^+ \rightarrow {}^1\Delta_g$ (1935 nm) fluorescence. A Nd:YAG laser (Brilliant) from Quantel with frequency tripling (4 ns, 355 nm) was used as the excitation source. The emissions were focused through the three observation ports of the sample housing by means of aspherical condensor lenses (focal length = 42 mm, diameter = 48 mm, Spindler & Hoyer) onto three different filter/detectors combinations: (1) interference filter (IF 764 nm, half width, hw = 19 nm) with photomultiplier (PM R1464 Hamamatsu), (2) IF 1940 nm (hw = 70 nm) and antireflection coated Ge disk with liquid N_2-cooled InAs diode J12-D and preamplifier PA7 (EG&G Judson), and (3) IF 1275 (hw = 40 nm) with fast liquid-N_2 cooled Ge diode (North Coast EO 817P). The response functions $P_{Ge}(t)$ and $P_{PM}(t)$ of Ge detector and PM to the laser pulse were recorded monitoring the fluorescence of erythrosin B (fluorescence lifetime in water 78 ps)[19] with the corresponding detectors. These transient signals served as apparatus functions for the deconvolution of the respective time-resolved measurements. The very fast decaying background fluorescence of the samples at 765 nm was separated from the extremely weak but slowly decaying $O_2(^1\Sigma_g^+)$ phosphorescence by means of a difference technique. A solution of the respective sensitizer in benzene with identical absorbance at 355 nm was added to the sample up to a concentration of 7 vol % BNZ, which is sufficient to quench $O_2(^1\Sigma_g^+)$ practically completely, and the signal was measured again. Since the background signal is not affected by the addition of benzene, the difference $\Delta I_{765}(t)$ of both signals corresponds to the time-resolved emission of $O_2(^1\Sigma_g^+)$.[14] The laser pulse energy was measured deflecting a small portion of the laser light onto a fast Si diode as detector. The four signals were intermediatly stored with two transient digitizers (Gould 4072) and transferred to a PC for averaging (up to 128 times) and evaluation. The absorbances of the solutions with BPH/NAPH and with the reference sensitizer PHE were optically matched to 0.50 per cm at 355 nm. In the measurement of the BPH phosphorescence, the IF765 was replaced by an IF 448 filter, and the other two observation ports were closed. In these experiments, a very fast decaying background fluorescence was also observed. Again, a difference technique was used for the isolation of the slowly decaying BPH phosphorescence. Adding NAPH up to 0.2 M leads to very fast deactivation of the T_1 state of BPH by TT energy transfer, whereas the interfering signals remain unchanged. Therefore the difference of the signals recorded with and without NAPH corresponds to the pure time-resolved phosphorescence of BPH. With exception of the BPH phosphorescence experiment in deoxygenated solution (O_2 removal by Ar bubbling), all other emission experiments have been done with air-saturated solutions. All experiments have been performed at 23 °C, varying the laser pulse energy. Only energy-independent results are reported.

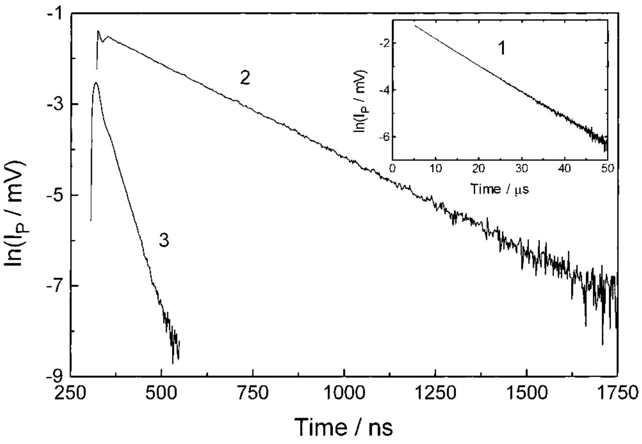

Figure 1. Logarithmic representation of the phosphorescence decay of BPH in CCl_4 at 23 °C in the absence of quenchers (1, $\tau_T = 9.0\ \mu s$), in air-saturated solution (2, $\tau_T^{O_2} = 244$ ns), and in air-saturated solution in the presence of [NAPH] = 4.0 mM (3, $\tau_T^{O_2,N} = 39$ ns).

Results and Discussion

Indirect Population of the T_1 State of the Secondary Sensitizer S2. A compromise has to be made for the optimum conditions of the quantitative measurement of the O_2 sensitization by S2 in the energy transfer cascade S1 → S2 → O_2 because of the very strong e–v deactivation of $O_2(^1\Sigma_g^+)$ by aromatic hydrocarbons sensitizers S2 and the limited detectability of $O_2(^1\Sigma_g^+)$. This optimum depends on the respective detection limit of $O_2(^1\Sigma_g^+)$, on the triplet state lifetime of S2, and on the efficiencies a and S_Δ of $O_2(^1\Sigma_g^+)$ and overall $O_2(^1\Delta_g)$ sensitization by S1 and can be specified by the efficiency f_T^{S2}(S1) of T_1 state population of S2 by TT energy transfer from S1. The optimum lies with our instrument for the S1/S2 sensitizer pair BPH/NAPH in the range $0.90 \lesssim f_T^{S2}(S1) \lesssim 0.95$. Several preparatory measurements have to be performed with each sensitizer system BPH/S2 to reproducibly adjust the experimental conditions. Equations 1–5 list the deactivation steps and the corresponding rate constants relevant in the energy transfer cascade, whereby S_0 indicates the singlet ground state

$$T_1(BPH) \rightarrow S_0(BPH) \qquad k_T^0(BPH) \tag{1}$$

$$T_1(BPH) + O_2 \rightarrow S_0(BPH) + O_2 \qquad k_T^{O_2}(BPH) \tag{2}$$

$$T_1(BPH) + S_0(S2) \rightarrow S_0(BPH) + T_1(S2) \qquad k_T^{S2}(BPH) \tag{3}$$

$$T_1(S2) \rightarrow S_0(S2) \qquad k_T^0(S2) \tag{4}$$

$$T_1(S2) + O_2 \rightarrow S_0(S2) + O_2 \qquad k_T^{O_2}(S2) \tag{5}$$

Reactions 1–3 can be measured via the phosphorescence of the primary sensitizer (see Figure 1).

We determined the average value of the T_1 state lifetime $\tau_T^0(BPH) = 1/(k_T^0(BPH))$ in the absence of O_2 to be $9.0 \pm 0.3\ \mu s$ in CCl_4. The mean value of the triplet lifetime in air-saturated solution $\tau_T^{O_2}(BPH) = 1/\{k_T^0(BPH) + k_T^{O_2}(BPH)[O_2]\}$

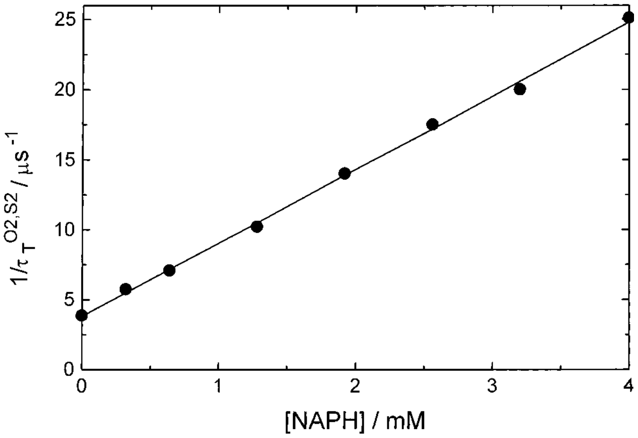

Figure 2. Stern−Volmer plot of the deactivation of $T_1(BPH)$ in air-saturated CCl_4.

amounts to 250 ± 7 ns. The lifetime is further reduced in the presence of S2: $\tau_T^{O_2,S2}(BPH) = 1/\{k_T^{O_2}(BPH)[O_2] + k_T^{S2}(BPH)[S2]\}$. The corresponding Stern−Volmer plot shown in Figure 2 yields as slope the rate constant of TT energy transfer from BPH to NAPH of $k_T^{S2}(BPH) = (5.2_4 \pm 0.2) \times 10^9$ M^{-1} s^{-1}.

Using eq 6, we calculate the efficiency of T_1 state population of S2 by TT energy transfer from BPH

$$f_T^{S2}(BPH) = k_T^{S2}(BPH)[S2]/\{1/\tau_T^{O_2}(BPH) + k_T^{S2}(BPH)[S2]\} \quad (6)$$

The fraction of $T_1(BPH)$ which is deactivated by O_2 results from

$$f_T^{O_2}(BPH) = k_T^{O_2}(BPH)[O_2]/\{1/\tau_T^{O_2}(BPH) + k_T^{S2}(BPH)[S2]\} \quad (7)$$

We performed the experiments with $[NAPH] = 8.0 \times 10^{-3}$ M, corresponding to the efficiencies $f_T^{S2}(BPH) = 0.913$ and $f_T^{O_2}(BPH) = 0.087$. It has to be considered that some of the singlet oxygen is sensitized by BPH. The efficiencies of the direct formation of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ in the quenching of the T_1 state of BPH by O_2 have been determined as $a = 0.10$ and $b = S_\Delta - a = 0.26$,[9] using the overall efficiency of $O_2(^1\Delta_g)$ sensitization of $S_\Delta = 0.36$.[20] Therefore, the efficiency of $O_2(^1\Sigma_g^+)$ sensitization and the overall efficiency of $O_2(^1\Delta_g)$ sensitization by BPH are rather small under these conditions ($[NAPH] = 8.0 \times 10^{-3}$ M) and amount to only $af_T^{O_2}(BPH) = 0.008_7$ and $S_\Delta f_T^{O_2}(BPH) = 0.031$.

Deactivation of the T_1 State of S2 by O_2 and Overall Efficiency of $O_2(^1\Delta_g)$ Sensitization. TT energy transfer from BPH to S2 occurs with the time constant $\tau_T^{O_2,S2}(BPH) = \{1/\tau_T^{O_2}(BPH) + k_T^{S2}(BPH)[S2]\}^{-1}$, which amounts to 22 ns with $[NAPH] = 8.0 \times 10^{-3}$ M. Finally, $T_1(S2)$ is deactivated by O_2 with lifetime $\tau_T^{O_2}(S2)$ leading to $O_2(^1\Sigma_g^+)$ formation with efficiency a^S and $O_2(^1\Delta_g)$ formation with the overall efficiency S_Δ^S.

The deactivation of $T_1(S2)$ can indirectly be monitored via the emission of its successor $O_2(^1\Delta_g)$. The rate constant of quenching of $O_2(^1\Sigma_g^+)$ by C_6H_6 amounts to $k_\Sigma = 6.6 \times 10^8$ M^{-1} s^{-1}.[14] With this value, it is calculated that the addition of 7 vol % BNZ reduces the $O_2(^1\Sigma_g^+)$ lifetime in pure CCl_4 by e−v deactivation from 130 ns in pure CCl_4 to 1.9 ± 0.2 ns. Hereby, $O_2(^1\Sigma_g^+)$ is completely and very quickly converted to $O_2(^1\Delta_g)$.[9,13] Therefore, the rise of the $O_2(^1\Delta_g)$ phosphorescence signal $I_{1275}^B(t)$, measured in the presence of 7 vol % BNZ at 1275 nm, corresponds in very good approximation to the decay of the triplet state of the secondary sensitizer as long as $\tau_T^{O_2}(S2)$ is at least about 1 order of magnitude larger than the actual lifetime $\tau_T^{O_2,S2}(BPH)$ (see Figure 3). The lifetime of triplet states of aromatic compounds with $\pi\pi^*$ character is rather long in liquids in the absence of O_2. For example, the triplet lifetime of naphthalene derivatives lies in the 100 μs range.[11] Thus, the efficiency of quenching of these T_1 states by O_2 is unity already in air-saturated solution. Equation 8 is derived for $I_{1275}^B(t)$, where τ_Δ represents the $O_2(^1\Delta_g)$ lifetime

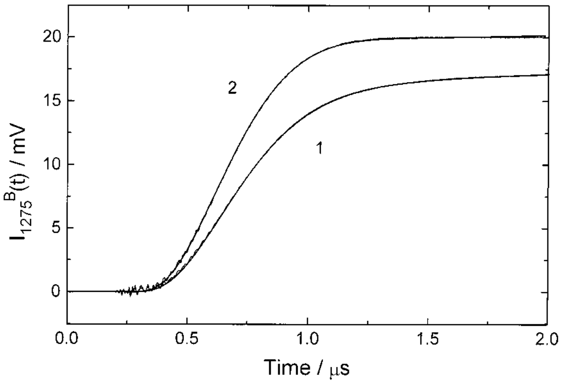

Figure 3. Rise of the $O_2(^1\Delta_g)$ phosphorescence signal at 1275 nm in air-saturated CCl_4 in the presence of 7 vol % BNZ and corresponding fits according to eq 8 for BPH/NAPH (1, $\tau_T^{O_2} = 327$ns) and PHE (2, $\tau_T^{O_2} = 220$ ns).

$$I_{1275}^B(t) = F_{1275}\tau_\Delta/(\tau_\Delta - \tau_T^{O_2})\{\exp(-t/\tau_\Delta) - \exp(-t/\tau_T^{O_2})\} \quad (8)$$

For the system BPH/S2, $F_{1275} = F_{1275}^{S,B} = c_{1275}(S_\Delta^S f_T^{S2}(BPH) + S_\Delta f_T^{O_2}(BPH))$ is valid with the apparatus constant c_{1275} and the triplet state lifetime of S2 $\tau_T^{O_2} = \tau_T^{O_2}(S2)$, respectively. $f_T^{S2}(BPH) = 0.913$ and $S_\Delta f_T^{O_2}(BPH) = 0.031$ result for [NAPH] $= 8.0 \times 10^{-3}$ M. For the directly excited reference sensitizer, which is PHE ($S_\Delta^R = 0.97$)[21] in our experiments, $F_{1275} = F_{1275}^{R,B} = c_{1275}0.97$ and $\tau_T^{O_2} = \tau_T^{O_2}(R)$ hold true. The fit of the convolution of the response function $P_{Ge}(t)$ with eq 8 with fixed $\tau_\Delta = 420$ μs (7 vol % BNZ in CCl_4) to the rise curves recorded with BPH/NAPH and PHE under identical experimental conditions results in the curves drawn in Figure 3. The average triplet lifetimes $\tau_T^{O_2}(S2) = 327 \pm 20$ ns of NAPH and $\tau_T^{O_2}(R) = 220 \pm 7$ ns of PHE, as well as $F_{1275}^{S,B}$ and $F_{1275}^{R,B}$, are obtained as fit parameters. Since the $T_1(\pi\pi^*)$ states of NAPH and PHE are completely quenched by O_2, the corresponding rate constants of deactivation of T_1 by O_2 are simply obtained from $k_T^Q = 1/(\tau_T^{O_2}[O_2])$ with $[O_2] = 2.3 \times 10^{-3}$ M in air-saturated CCl_4,[14] leading to $k_T^Q = (1.33 \pm 0.10) \times 10^9$ M^{-1} s^{-1} for NAPH. $S_\Delta^S = 0.880 \pm 0.035$ is calculated for NAPH by eq 9 and the average experimental results of $F_{1275}^{S,B}$ and $F_{1275}^{R,B}$

$$S_\Delta^S = (0.97F_{1275}^{S,B}/F_{1275}^{R,B} - S_\Delta f_T^{O_2}(BPH))/f_T^{S2}(BPH) \quad (9)$$

The Lifetime of $O_2(^1\Sigma_g^+)$. The lifetime τ_Σ of $O_2(^1\Sigma_g^+)$ was measured via the emission at 765 nm. The difference $\Delta I_{765}(t) = I_{765}(t) - I_{765}^B(t)$ of the emissions recorded under identical experimental conditions without and with 7 vol % BNZ represents in good approximation the actual $O_2(^1\Sigma_g^+)$ phosphorescence, which is emitted with the extremely small quantum yield of about 10^{-7} in pure CCl_4.[22,23] However, due to the very high intensity of scattered light and residual fluorescence of sensitizer and impurities, $\Delta I_{765}(t)$ data are missing in the first

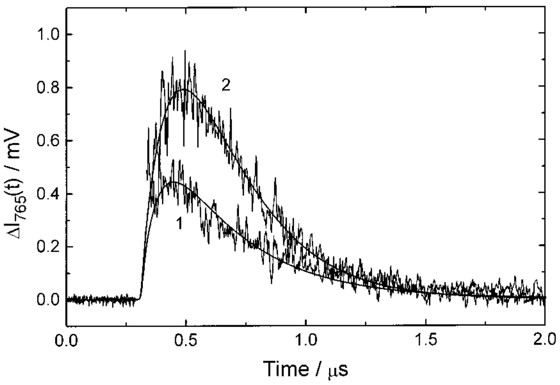

Figure 4. Rise and decay of the $O_2(^1\Sigma_g^+)$ phosphorescence signal at 765 nm in air-saturated CCl_4 with corresponding fits according to eq 10 for BPH/NAPH (1, $\tau_\Sigma^S = 65$ ns) and PHE (2, $\tau_\Sigma^R = 137$ ns) (see the discussion of τ_Σ^S in text).

40 (PHE) and 70 (BPH/NAPH) ns. Figure 4 plots the corresponding traces for BPH/NAPH and PHE.

Equation 10 is derived for $\Delta I_{765}(t)$

$$\Delta I_{765}(t) = F_{765}\tau_\Sigma/(\tau_\Sigma - \tau_T^{O_2})\{\exp(-t/\tau_\Sigma) - \exp(-t/\tau_T^{O_2})\} \qquad (10)$$

$F_{765} = F_{765}^S = c_{765}f_\Sigma^B(a^S f_T^{S2}(\mathrm{BPH}) + af_T^{O_2}(\mathrm{BPH}))$ is valid for the system BPH/S2. c_{765} is the apparatus constant, $f_\Sigma^B = f_\Sigma^{B,S}$ the fraction of $O_2(^1\Sigma_g^+)$ being quenched by BNZ in the solution with S2, a^S the efficiency of $O_2(^1\Sigma_g^+)$ sensitization by $T_1(S2)$, $\tau_\Sigma = \tau_\Sigma^S$, and $\tau_T^{O_2} = \tau_T^{O_2}(S2)$. $f_T^{S2}(\mathrm{BPH}) = 0.913$ and $af_T^{O_2}(\mathrm{BPH}) = 0.008_7$ result for [NAPH] = 8.0×10^{-3} M. For the solution containing the reference $F_{765} = F_{765}^R = c_{765}f_\Sigma^B a^R$ holds true, with $f_\Sigma^B = f_\Sigma^{B,R}$ being the fraction of $O_2(^1\Sigma_g^+)$ quenched by BNZ in the reference solution, $a^R = 0.60$ for PHE,[10] $\tau_\Sigma = \tau_\Sigma^R$, and $\tau_T^{O_2} = \tau_T^{O_2}(R)$.

If the triplet lifetime $\tau_T^{O_2}(R) = 220$ ns of PHE is kept fixed, the fit of the convolution of eq 10 with the response function $P_{PM}(t)$ to the experimental trace 2 results in the curve drawn in Figure 4, which describes the experimental trace, and in the fit parameter $\tau_\Sigma^R = 137 \pm 10$ ns. $\tau_\Sigma^S = 65$ ns is obtained for the solution with BPH/NAPH if $\tau_T^{O_2}(S2) = 327$ ns is kept constant. Since the shorter lifetime always determines the rising part of a biexponential rise and decay curve and since, furthermore, usually $\tau_\Sigma < \tau_T^{O_2}$ holds true, it is the early part of the transient curves of Figure 4 which contains most information about τ_Σ^R and τ_Σ^S. Unfortunately, in this region, data are missing. That is the reason the uncertainty of τ_Σ increases significantly below about 40 ns with PHE (emission data missing in the first 40 ns) but already much earlier with BPH/NAPH (data missing in the first 70 ns). Consequently, the uncertainty of $\tau_\Sigma^S = 65$ ns is considerable.

For comparison, an estimate of τ_Σ could be derived from the experimentally determined rate constants of $O_2(^1\Sigma_g^+)$ quenching by S1 and S2, considering the value of $\tau_\Sigma = 130$ ns in pure CCl_4. With $k_\Sigma^Q(\mathrm{BPH}) = 1.1 \times 10^9$ M^{-1} s^{-1}, [BPH] = 0.005 M, $k_\Sigma^Q(\mathrm{NAPH}) = 8.8 \times 10^8$ M^{-1} s^{-1}, and [NAPH] = 8.0×10^{-3} M, we estimate $\tau_\Sigma^S = 49$ ns, which differs distinctly from the above obtained 65 ns. Therefore, additional experiments are necessary to obtain more certainty about τ_Σ^S. Comparative measurements of the $O_2(^1\Sigma_g^+) \rightarrow O_2(^1\Delta_g)$ emission $I_{1935}(t)$ yield further information about τ_Σ. The integrated signal INT_{1935} is directly proportional to τ_Σ

$$\mathrm{INT}_{1935} = \mathrm{F}_{1935}\tau_\Sigma \qquad (11)$$

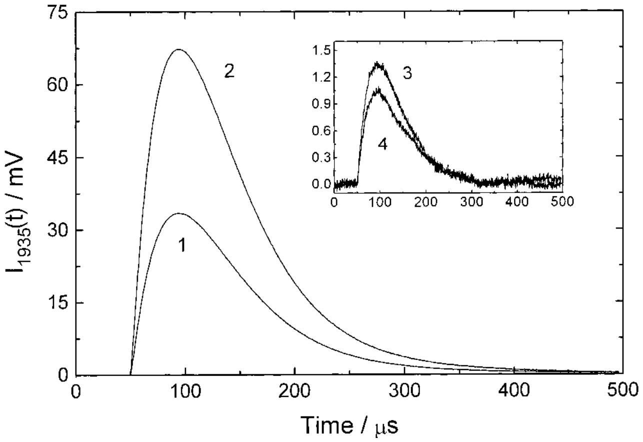

Figure 5. $O_2(^1\Sigma_g^+)$ phosphorescence signals at 1935 nm in air-saturated CCl_4 for BPH/NAPH (1) and PHE (2). The inset shows the corresponding signals for BPH/NAPH (3) and PHE (4) in the presence of 7 vol % BNZ. The shape of the traces $I_{1935}(t)$ is solely determined by the response of the detector.

For the system BPH/S2, $F_{1935} = F_{1935}^S = c_{1935}(a^S f_T^{S2}(\mathrm{BPH}) + af_T^{O_2}(\mathrm{BPH}))$ holds true with apparatus constant c_{1935} and $\tau_\Sigma = \tau_\Sigma^S$. $F_{1935} = F_{1935}^R = c_{1935}0.60$, and $\tau_\Sigma = \tau_\Sigma^R$ for the reference solution with PHE. The instrument allows a rather good signal-to-noise ratio of $I_{1935}(t)$ still in the presence of 7 vol % BNZ (see Figure 5).

We calculate that τ_Σ is decreased by e−v deactivation from $\tau_\Sigma^R = 130$ ns in pure CCl_4 to $\tau_\Sigma^{R,B} = 1.90$ ns with 7 vol % BNZ. If additional quenching of $O_2(^1\Sigma_g^+)$ by sensitizers occurs, as in the case of the BPH/NAPH system, we calculate that the addition of 7 vol % BNZ reduces τ_Σ from the above derived estimate $\tau_\Sigma^S = 49$ ns to $\tau_\Sigma^{S,B} = 1.84$ ns. Since $\tau_\Sigma^{S,B} \approx \tau_\Sigma^{R,B}$ holds approximately true and since sample and reference solution are always prepared from the same CCl_4 stock, eq 12 can be used for the determination of τ_Σ^S

$$\tau_\Sigma^S = \tau_\Sigma^R F_{1935}^S F_{1935}^{R,B}/(F_{1935}^{S,B} F_{1935}^R) \qquad (12)$$

We obtain $\tau_\Sigma^S = 53$ ns from the experimental data of Figure 5 by eq 12. The uncertainty of this indirect method is estimated to be with ±10% much smaller than that of the direct method if emission data are lacking for large time intervals directly after laser excitation. Then, only the indirectly determined data are taken for evaluation.

Efficiency a^S of Sensitization of $O_2(^1\Sigma_g^+)$ by $T_1(S2)$. $O_2(^1\Sigma_g^+)$ can indirectly be measured via the emission of $O_2(^1\Delta_g)$.[10] $O_2(^1\Sigma_g^+)$ is completely converted with time constant τ_Σ to $O_2(^1\Delta_g)$ by e−v deactivation.[9,13] Therefore, the rise of the $O_2(^1\Delta_g)$ emission at 1275 nm is faster in the presence of 7 vol % BNZ than in its absence. The difference $\Delta I_{1275}(t) = I_{1275}^B(t) - I_{1275}(t)$ of the emissions recorded with and without BNZ corresponds to the rise and decay of $O_2(^1\Sigma_g^+)$ recorded via the emission of its successor $O_2(^1\Delta_g)$ (see Figure 6).

Equation 13 holds true as long as the deactivation of $O_2(^1\Delta_g)$ can be neglected on the time scale of measurement (2.5 μs)

$$\Delta I_{1275}(t) = F'_{1275}\tau_\Sigma/(\tau_\Sigma - \tau_T^{O_2})\{\exp(-t/\tau_\Sigma) - \exp(-t/\tau_T^{O_2})\} \qquad (13)$$

Integration of $\Delta I_{1275}(t)$ in the limits from $t = 0$ to $t = \infty$ yields $\mathrm{INT}\Delta_{1275}$

$$\mathrm{INT}\Delta_{1275} = F'_{1275}\tau_\Sigma \qquad (14)$$

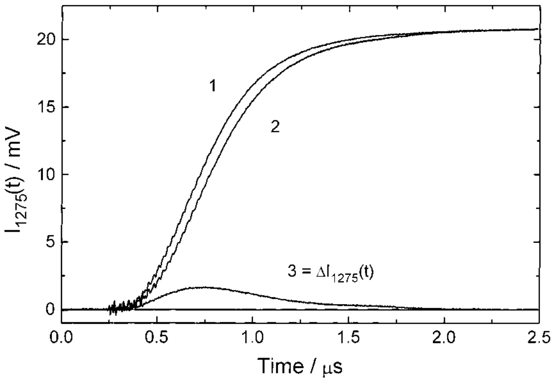

Figure 6. Rise of the $O_2(^1\Delta_g)$ phosphorescence signal at 1275 nm in air-saturated CCl_4 in the presence (1) and absence (2) of 7 vol % BNZ for BPH/NAPH; difference signal (3).

TABLE 1

sensitizer	$\tau_T^{O_2}$, ns	$10^{-9}k_T^Q$,$M^{-1}\,s^{-1}$	S_Δ	a
PHE	220 ± 15	2.00 ± 0.15	0.97 ± 0.03	0.60 ± 0.04
NAPH	327 ± 20	1.33 ± 0.10	0.880 ± 0.035	0.802 ± 0.090

$F'_{1275} = F'_{1275}{}^S = c_{1275}\, f_\Sigma{}^{B,S}\, (a^S f_T{}^{S2}(\mathrm{BPH}) + a f_T{}^{O_2}(\mathrm{BPH}))$ is valid for BPH/S2 and $F'_{1275} = F'_{1275}{}^R = c_{1275}\, f_\Sigma{}^{B,R} 0.60$ for the reference PHE. The fraction $f_\Sigma{}^B$ of $O_2(^1\Sigma_g^+)$ being quenched by the added BNZ depends on the value of τ_Σ in the solution without BNZ and is larger for the reference solution where no additional deactivation by the sensitizers BPH and NAPH takes place. $f_\Sigma{}^B$ is determined using

$$f_\Sigma{}^B = (\mathrm{INT}_{1935} - \mathrm{INT}_{1935}{}^B)/\mathrm{INT}_{1935} \tag{15}$$

From the data given in Figure, 5 we calculate that $f_\Sigma{}^{B,S} = 0.960$ for BPH/NAPH and $f_\Sigma{}^{B,R} = 0.984$ for PHE. Comparative measurements of $\mathrm{INT}\Delta_{1275}$ with BPH/NAPH and PHE allow the determination of the efficiency a^S

$$a^S = \{0.60(\mathrm{INT}\Delta_{1275}{}^S f_\Sigma{}^{B,R} \tau_\Sigma{}^R)/(\mathrm{INT}\Delta_{1275}{}^R f_\Sigma{}^{B,S} \tau_\Sigma{}^S) - a f_T{}^{O_2}(\mathrm{BPH})\}/f_T{}^{S2}(\mathrm{BPH}) \tag{16}$$

An independent value of a^S is obtained in comparative measurements of the integrally detected emissions of $O_2(^1\Sigma_g^+)$ at 1935 nm of BPH/NAPH and PHE by

$$a^S = \{0.60(\mathrm{INT}_{1935}{}^S \tau_\Sigma{}^R)/(\mathrm{INT}_{1935}{}^R \tau_\Sigma{}^S) - a f_T{}^{O_2}(\mathrm{BPH})\}/f_T{}^{S2}(\mathrm{BPH}) \tag{17}$$

In four independent investigations, which all have been carried out varying the laser pulse energy, we obtained as mean value $a^S = 0.802 \pm 0.09$. Table 1 lists the primary results for PHE and NAPH.

Rate Constants of Formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ in the Quenching of Triplet States by O_2. The rate constants of direct formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ can simply be obtained as $k_T{}^{1\Sigma} = a k_T{}^Q$, $k_T{}^{1\Delta} = (S_\Delta - a)k_T{}^Q$, and $k_T{}^{3\Sigma} = (1 - S_\Delta)k_T{}^Q$ as long as the values of $k_T{}^Q$ are at least 1 order of magnitude smaller than the diffusion controlled rate constant, which amounts to $k_{\mathrm{diff}} = 2.72 \times 10^{10}\ M^{-1}\ s^{-1}$ in CCl_4.[24] Taking the average results of $a^S = 0.802$, $S_\Delta{}^S = 0.880$, and $k_T{}^Q = 1.33 \times 10^9\ M^{-1}\ s^{-1}$, we obtain in this simple evaluation for naphthalen as triplet sensitizer $k_T{}^{1\Sigma} = 1.07 \times 10^9\ M^{-1}\ s^{-1}$, $k_T{}^{1\Delta} = 1.04 \times 10^8\ M^{-1}\ s^{-1}$, and $k_T{}^{3\Sigma} = 1.60 \times 10^8\ M^{-1}\ s^{-1}$. Only if the value of $k_T{}^Q$ approaches the value of k_{diff} does the calculation become slightly more complex. The corresponding evaluation will be discussed in the following paper, where all results of the naphthalene sensitizers are presented.[25]

Since $k_T{}^{1\Delta}$ and $k_T{}^{3\Sigma}$ result in part from small differences of efficiencies, the discussion of the experimental uncertainties is very important in the consideration of error limits. The relative uncertainties dx/x of the primary data amount to ± 0.10 for $k_T{}^Q$, ± 0.04 for S_Δ, and ± 0.11 for a^S. The uncertainty of a^S is mainly determined by the experimental error $dx/x = 0.10$ of the ratio $\tau_\Sigma{}^R/\tau_\Sigma{}^S$ but not by the magnitude of a^S. Thus, error propagation leads to a constant uncertainty of $k_T{}^{1\Sigma}$ of $dx/x = 0.15$. The uncertainties of $k_T{}^{1\Delta}$ and $k_T{}^{3\Sigma}$, however, are not constant. They strongly depend on the magnitude of the efficiencies $S_\Delta{}^S$ and a^S. With $b^S = S_\Delta{}^S - a^S$, $dS_\Delta = 0.04S_\Delta$, and $da^S = 0.11a^S$, we derive $db^S/b^S = \{(0.04S_\Delta{}^S/(S_\Delta{}^S - a^S))^2 + (0.11a^S/(S_\Delta{}^S - a^S))^2\}^{0.5}$, indicating a drastic increase of the uncertainty db^S/b^S with the decreasing difference $S_\Delta{}^S - a^S$. For the uncertainty of the efficiency of the formation of $O_2(^3\Sigma_g^-)$, $d(1 - S_\Delta{}^S)/(1 - S_\Delta{}^S) = 0.04S_\Delta{}^S/(1 - S_\Delta{}^S)$ similarly holds true. Therefore, depending on the magnitude of the differences $S_\Delta{}^S - a^S$ and $1 - S_\Delta{}^S$, very different and partially large relative errors may result for b^S and $1 - S_\Delta{}^S$ and, consequently, for $k_T{}^{1\Delta}$ and $k_T{}^{3\Sigma}$. This is particularly well demonstrated for the example of the sensitizer naphthalene, for which we obtain uncertainties dx/x of 0.15 for $k_T{}^{1\Sigma}$, 1.26 for $k_T{}^{1\Delta}$, and 0.31 for $k_T{}^{3\Sigma}$. It does not appear meaningful to calculate the error limits of a definitely positive quantity x for which dx is larger than x simply as $x(1 \pm dx/x)$, since then the lower error limit would be in the negative range. Instead, we prefer to estimate the upper and lower limits by multiplying x with the factors $(1 + dx/x)$ and $1/(1 + dx/x)$, respectively. This procedure corresponds to equally positive and negative error bars on a logarithmic scale. Through this, we finally obtain for NAPH: $k_T{}^{1\Sigma} = (1.07 + 0.16/{-0.14}) \times 10^9\ M^{-1}\ s^{-1}$, $k_T{}^{1\Delta} = (1.0 + 1.3/{-0.6}) \times 10^8\ M^{-1}\ s^{-1}$, and $k_T{}^{3\Sigma} = (1.6 + 0.5/{-0.4}) \times 10^8\ M^{-1}\ s^{-1}$.

Conclusion

A method is described for the determination of the rate constants of the competitive formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$ in the deactivation of the triplet state by O_2 of sensitizers with incomplete intersystem crossing. This technique allows for the study of a wider range of sensitizers of singlet oxygen and is used in the following article for the investigation of a series of naphthalene sensitizers of different oxidation potential but almost constant triplet energy.[25] There it is shown that two deactivation channels exist both leading to the formation of $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$, and $O_2(^3\Sigma_g^-)$**.** One originates from excited complexes without significant charge-transfer character, the other from exciplexes with partial charge transfer.

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References and Notes

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

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

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

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

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

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

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

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

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

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

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

(12) Schmidt, R. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 794.

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

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

(15) Chou, P.-T.; Wei, G.-T., Lin, C. H.; Wei, C.-Y.; Chang, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 3031.

(16) Losev, A. P.; Bachilo, S. M.; Nichiporovich, I. N. *J. Appl. Spectrosc.* **1998**, *65*, 1.

(17) Schmidt, R.; Shafii, F.; Hild, M. *J. Phys. Chem. A* **1999**, *103*, 2599.

(18) Keszthelyi, T.; Weldon, D.; Anderson, T. N.; Poulsen, T. D.; Mikkelsen, K. V.; Ogilby, P. R. *Photochem. Photobiol.* **1999**, *70*, 531.

(19) Yu, W.; Pellegrino, F.; Grant, M.; Alfano, R. R. *J. Chem. Phys.* **1977**, *67*, 1766.

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

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

(22) Schmidt, R.; Bodesheim, M. *J. Phys. Chem.* **1995**, *99*, 15919.

(23) Chou, P.-T.; Chen, Y.-C., Wei, C.-Y.; Chen, S.-J.; Lu, H.-L.; Wei, T.-H. *J. Phys. Chem. A.* **1997**, *101*, 8581.

(24) The viscosities of cyclohexane and CCl_4 amount to 0.975 and 0.969 mPas at 20 °C.[13] Therefore, we take the value $k_{diff} = 2.72 \times 10^{10}$ M^{-1} s^{-1} derived by Wilkinson et al. in ref 7 for cyclohexane to be also valid for CCl_4.

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