J. Phys. Chem. A **2000,** *104,* 3177−3180

Time-Resolved Determination of the Quantum Yield of Singlet Oxygen Formation by Tetraphenylporphine under Conditions of Very Strong Quenching[†]

Reinhard Schmidt*,[‡] and Charles Tanielian[§]

Institut für Physikalische und Theoretische Chemie, J. W. Goethe-Universität, Marie-Curie-Strasse 11, D60439 Frankfurt am Main, Germany, and Laboratoire de Photochimie, Ecole Européenne de Chimie Polymères et Matériaux, 25, rue Becquerel, F67087 Strasbourg Cedex 2, France

Received: November 16, 1999; In Final Form: January 31, 2000

Time-resolved measurements of the $O_2(^1\Delta_g)$ singlet oxygen luminescence sensitized by tetraphenylporphine (TPP) have been performed in the presence of varying concentrations of the $O_2(^1\Delta_g)$ trap tetramethylethylene (TME). Although the $O_2(^1\Delta_g)$ luminescence signal at 1275 nm is partially overlapped by residual sensitizer fluorescence, we still achieved accurate measurements of lifetimes τ_Δ of $O_2(^1\Delta_g)$ and quantum yields Q_Δ of $O_2(^1\Delta_g)$ sensitization even if τ_Δ is reduced to about 200 ns. These quantitative measurements (i) yield $Q_\Delta = 0.78 \pm 0.04$ in air-saturated benzene, which corrects the average $Q_\Delta = 0.6 \pm 0.1$ of the literature values obtained with this technique but is identical to the value $Q_\Delta = 0.80$ previously found with TME by the photostationary state method, (ii) confirm that the fraction S_Δ of triplets quenched by O_2 giving rise to $O_2(^1\Delta_g)$ is nearby unity in benzene, and (iii) exclude a relatively long-lived nonluminescent complex being highly reactive toward TME, formed from $O_2(^1\Delta_g)$ and TPP, which was previously proposed, precisely to explain the difference between the values obtained by the two techniques.

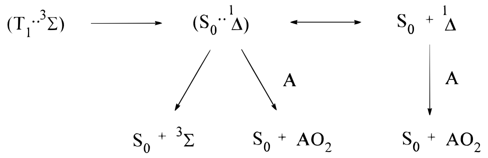
Introduction

Porphine derivatives are well-known to be highly effective photosensitizers of singlet oxygen $O_2(^1\Delta_g)$.[1] They have important applications in both natural and artificial photosystems and can be employed to produce $O_2(^1\Delta_g)$ for therapeutic purposes. For most of the applications, it is necessary to establish precise quantum yields Q_Δ for the sensitized production of $O_2(^1\Delta_g)$. Two experimental techniques are commonly used to determine the values of Q_Δ: time-resolved measurements of the near-infrared luminescence of $O_2(^1\Delta_g)$ (TL) and steady-state photochemical methods (SP) that depend on chemical trapping of the product or depletion of the initial oxygen concentration.[1]

The first determination of Q_Δ for 5,10,15,20-tetraphenylporphine (TPP) was made under steady-state excitation using the oxygen consumption method, and values of $Q_\Delta^{SP} = 0.89$ and 0.88 were found in oxygen-saturated benzene and toluene, respectively.[2] With the development of TL techniques, several values of Q_Δ^{TL} have been reported for TPP in air-saturated benzene.[1,3] Their average $Q_\Delta^{TL} = 0.6 \pm 0.1$ is significantly lower than the previously obtained value of Q_Δ^{SP}.

These differences led Tanielian and Wolff to measuring the quantum yields for the formation of the triplet excited state and of $O_2(^1\Delta_g)$, by both steady-state and pulsed laser excitation, for various porphine derivatives in benzene or methanol under different concentrations of O_2.[4] In most cases, an excellent agreement was observed between the two experimental techniques. However, for certain tetraphenylporphines in benzene, the SP method gave Q_Δ values that were markedly higher than those obtained by TL. The largest discrepancy was observed for TPP, for which in air-saturated benzene $Q_\Delta^{SP} = 0.80$ and $Q_\Delta^{TL} = 0.56$ was found, thus confirming the precedently published values. Furthermore, from the values of the quantum yield of the triplet state population determined by the two techniques,[5] it was deduced that the efficiency of singlet oxygen formation in the quenching of TPP triplet state by O_2 apparently depends on the method used: $S_\Delta = 0.8$ (TL) versus 1.0 (SP).

SCHEME 1



To resolve this contradiction, it was proposed that a nonluminescent exciplex $(S_0{\cdot\cdot}^1\Delta)$ of ground-state TPP and $O_2(^1\Delta_g)$ is formed on the way of $O_2(^1\Delta_g)$ sensitization, which is in equilibrium with S_0 and $O_2(^1\Delta_g)$ but which has an additional deactivation path leading to formation of ground-state oxygen $O_2(^3\Sigma_g^-)$; see Scheme 1.[4]

The scavenger A (=TME), which deactivates $O_2(^1\Delta_g)$ exclusively by chemical reaction,[6−8] was used in 0.12 M concentration to trap $O_2(^1\Delta_g)$ completely in the Q_Δ^{SP} measurements. It was assumed that, if the exciplex readily reacts with TME and has a sufficient lifetime, the exciplex deactivation $(S_0{\cdot\cdot}^1\Delta) \rightarrow S_0 + {}^3\Sigma$ could completely be suppressed at this high scavenger concentration. This would lead to a value of Q_Δ^{SP} being as large as Q_T and distinctly larger than the value of Q_Δ^{TL}, which normally is determined in the absence of A by monitoring the $O_2(^1\Delta_g)$ luminescence relative to a reference.

Exciplexes with O_2 have been postulated in the singlet oxygen literature for a variety of processes, such as singlet oxygen sensitization,[9−15] singlet oxygen quenching,[16−20] and photooxygenation.[21−26] Up to now only indirect evidence has been found for their existence. However, the presence of the

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[†] Dedicated to Professor K. Schaffner on occasion of his retirement.

[*] To whom correspondence should be addressed. E-mail: R.Schmidt@chemie.uni-frankfurt.de.

[‡] J. W. Goethe-Universität.

[§] Ecole Européenne de Chimie Polymères et Matériaux.

10.1021/jp994057n CCC: $19.00

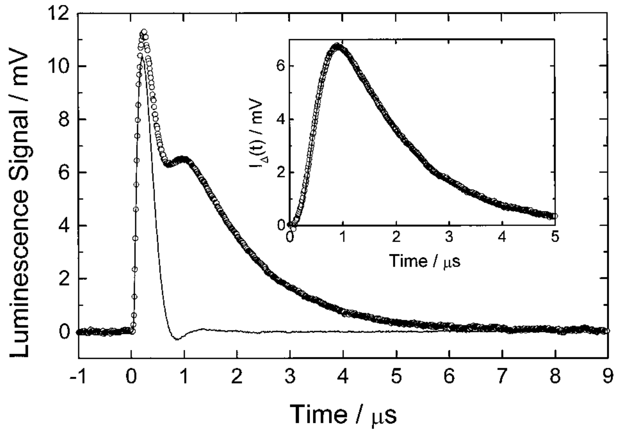

Figure 1. Overall luminescence signal at 1275 nm of a solution of TPP in air-saturated benzene at [TME] = 0.024 M (open circles); scaled apparatus function (solid curve). The inset shows the pure $O_2(^1\Delta_g)$ luminescence (open circles) and the corresponding fit (solid curve). Fit parameters: $\tau_\Delta = 1.12$ μs and $\tau_T = 300$ ns. For details see text.

postulated reactive exciplex of $O_2(^1\Delta_g)$ and TPP could actually experimentally be proved. Since the values of Q_Δ^{SP} are equal to the values of Q_T, the exciplex $(S_0{\cdot\cdot}{}^1\Delta)$, being the precursor of $O_2(^1\Delta_g)$, should already be completely scavenged at [TME] = 0.12 M. Thus, the quantum yield of $O_2(^1\Delta_g)$ sensitization determined via the $O_2(^1\Delta_g)$ luminescence should be much smaller at [TME] = 0.12 M compared with the value of Q_Δ^{TL} determined at [TME] = 0, if a reactive exciplex is really the reason for the finding $Q_\Delta^{SP} > Q_\Delta^{TL}$. To verify this hypothethis, we have initiated an experimental study of the $O_2(^1\Delta_g)$ sensitization by TPP in benzene in the presence of varying concentrations of TME by time-resolved luminescence techniques.

Experimental Section

Tetramethylethylene (TME, = 2,3-dimethyl-2-butene, Aldrich, 99+%), TPP (Aldrich, 97%), and C_6H_6 (Aldrich, 99+%) were taken as supplied. The singlet oxygen sensitizer phenalenone (PHE, Aldrich, 97%) was purified by column chromatography (CH_2Cl_2/silica gel). The setup for the time-resolved measurements of the $O_2(^1\Delta_g)$ emission has been described.[13,26,27] Some changes have been made. Particular care has been taken to improve the emission light collection efficiency by means of aspherical condensor lenses (focal length = 42 mm, diameter = 48 mm, Spindler und Hoyer). A Nd:YAG laser (Brilliant) from Quantel with frequency tripling (4 ns, 355 nm) was used as the excitation source. The detector was a fast liquid-N_2 cooled Ge-diode (North Coast EO 817P) with an 1275 nm interference filter (hbw = 40 nm). The diode signals were intermediately stored with a transient digitizer (Gould 4072) and transferred to a PC for averaging (50−128 times) and evaluation. The emission experiments have been done with air-saturated solutions in benzene at 23 °C by varying the excitation pulse energy. The purified TME does not absorb at 355 nm. The absorbances of the solutions with the sensitizers TPP or PHE amounted to 0.46/cm at 355 nm and were kept constant in the TME quenching experiments.

Results and Discussion

The presence of TME drastically reduces the $O_2(^1\Delta_g)$ lifetime, which amounts to $\tau_\Delta = 30.2$ μs in pure benzene. Figure 1 shows the luminescence signal recorded with [TME] = 0.024 M in benzene at 1275 nm.

Two maxima can be discerned. The first results from the fluorescence of the sensitizer TPP, which still extends to 1275 nm, the second has to be attributed to the $O_2(^1\Delta_g)$ luminescence. Thus, the problem of separating the pure rise and decay signal of $O_2(^1\Delta_g)$ has to be solved. The luminescence of $O_2(^1\Delta_g)$ is completely suppressed in the presence of [TME] = 2 M. The remaining signal corresponds to the TPP fluorescence and is given in Figure 1 as a solid curve. This signal is used as the apparatus function comprising the actual instrumental response (laser pulse, Ge-diode, digitizer) and the delayed population of the TPP triplet state occurring within the S_1 state lifetime of TPP of about 14 ns.[28] The TPP fluorescence signal of Figure 1 is scaled such that the initial increase of the overall signal (not of its maximum) is reproduced. If it is properly scaled, then the difference between the overall signal and the scaled TPP fluorescence signal starts slightly after time zero (ignition of the laser pulse) and has no significant negative contributions; see the inset of Figure 1. Then, the difference signal corresponds to the pure $O_2(^1\Delta_g)$ luminescence $I_\Delta(t)$. The rise and decay of $O_2(^1\Delta_g)$ following instantaneous excitation of a triplet state of lifetime τ_T is given by

$$[^1\Delta]_t = \alpha E_P Q_\Delta \tau_\Delta/(\tau_\Delta - \tau_T)\{\exp(-t/\tau_\Delta) - \exp(-t/\tau_T)\} \quad (1)$$

where α and E_P are a proportionality constant and the excitation pulse energy. Using nonlinear least-squares fitting routines,[29] it is actually possible to fit the convolution of the apparatus function with eq 1 to the difference curve $I_\Delta(t)$ of Figure 1. The fit is shown in the inset of Figure 1 as a solid curve. We obtain as fit parameters $\tau_\Delta = 1.12$ μs and $\tau_T = 300$ ns for TPP in air-saturated benzene. The same value of τ_T is obtained in the absence of TME (curve not shown). With $[O_2] = 1.68 \times 10^{-3}$ M, calculated from the molar fraction of O_2 in benzene of $x = 8.06 \times 10^{-4}$ at 23 °C considering the vapor pressure of benzene of 87 Torr,[30,31] the rate constant of quenching of the triplet state of TPP is obtained as $k_Q^T = (2.0 \pm 0.1) \times 10^9$ M^{-1} s^{-1}.[32] This value agrees perfectly with the literature value $k_Q^T = 1.8 \times 10^9$ M^{-1} s^{-1},[4] if the too large value of $[O_2] = 1.9 \times 10^{-3}$ M given by Murov et al.,[33] which was used for its evaluation, is taken into account. Time-resolved experiments monitoring a similarly fast rise and decay of $O_2(^1\Delta_g)$ have been published by Krasnovsky and co-workers as well as by Nonell et al., who determined with *meso*-tetrasulfonatophenylporphine as sensitizer in oxygen-saturated H_2O $\tau_T = 0.6$ μs and $\tau_\Delta = 3.1$ μs and in air-saturated H_2O $\tau_T = 2.1$ μs and $\tau_\Delta = 3.6$ μs, respectively.[34,35]

The lifetime τ_Δ and in consequence the contribution of the $O_2(^1\Delta_g)$ emission to the overall luminescence signal is further decreased at higher concentrations of TME. Figure 2 shows the signal recorded at the maximum concentration [TME] = 0.12 M, the concentration at which the Q_Δ^{SP} measurements had been performed.

Subtracting the scaled TPP signal yields the pure rise and decay signal of $O_2(^1\Delta_g)$ given in the inset of Figure 2. The fit of the convolution of the apparatus function with eq 1 to the difference curve, which is drawn in the inset, was obtained with fixed $\tau_T = 300$ ns and resulted in $\tau_\Delta = 209$ ns. Two independent series of measurements with varying concentrations of TME have been performed. Very similar results have been found. The variation of the mean values of $1/\tau_\Delta$ with [TME] is shown in the Stern−Volmer plot, Figure 3.

A very smooth linear correlation is observed. The rate constant of reaction of TME with $O_2(^1\Delta_g)$ is obtained as slope of the linear least-squares fit: $k_R = (3.6 \pm 0.2) \times 10^7$ M^{-1} s^{-1}. This result compares very well with the k_R values of 3.6×10^7

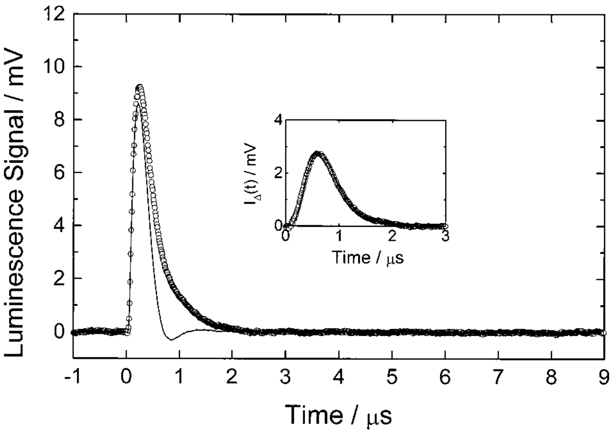

Figure 2. Overall luminescence signal at 1275 nm of a solution of TPP in air-saturated benzene at [TME] = 0.120 M (open circles); scaled apparatus function (solid curve). The inset shows the pure $O_2(^1\Delta_g)$ luminescence (open circles) and the corresponding fit (solid curve). Fit parameter: $\tau_\Delta = 209$ ns. Fixed parameter: $\tau_T = 300$ ns. For details see text.

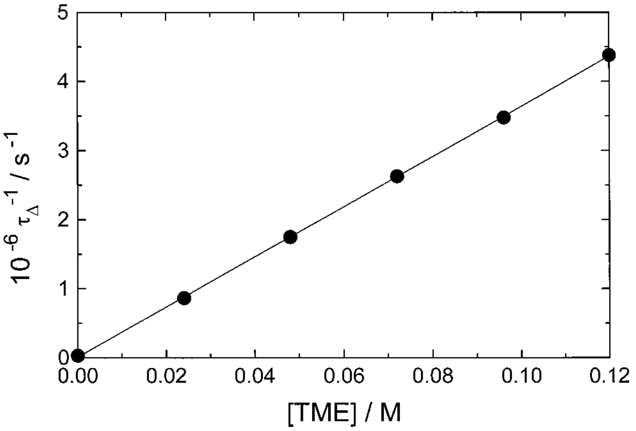

Figure 3. Stern−Volmer plot of reciprocal $O_2(^1\Delta_g)$ lifetimes; the slope of the linear least-squares fit is $k_R = (3.6 \pm 0.2) \times 10^7$ M^{-1} s^{-1}. For details see text.

and 3.3 × 10^7 M^{-1} s^{-1} determined in toluene.[17,36] The agreement of our results of k_Q^T and k_R with the literature data confirms the validity of the method of separation of the overlapping emissions and the convolution procedures. In fact, we have verified by calculation that the convolution of the apparatus function with a sum of two exponential decays leads to the same result as the sum of two single convolutions of the apparatus function with the respective monoexponential decays. Thus, we demonstrate that reliable measurements of the $O_2(^1\Delta_g)$ rise and decay are possible under conditions of very strong quenching of $O_2(^1\Delta_g)$, reducing τ_Δ to about 200 ns, even if the sensitizer fluorescence extends to 1275 nm and parially overlaps the $O_2(^1\Delta_g)$ luminescence.

The fact that a signal of $O_2(^1\Delta_g)$ is observed even at the highest value of [TME] already qualitatively indicates that the exciplex ($S_0{\cdot\cdot}{}^1\Delta$) is not completely trapped by TME. However, the measurements can also quantitatively be evaluated. Integration of eq 1 from time zero to infinity yields

$$\mathrm{INT}_\Delta = \alpha E_P Q_\Delta^{TL} \tau_\Delta \qquad (2)$$

Equation 2 allows the evaluation of relative quantum yields $Q_{\Delta,r}^{TL}$ of $O_2(^1\Delta_g)$ sensitization determined by time-resolved luminescence (TL) as a function of [TME], if the integrals INT'_Δ of the signals $I_\Delta(t)$ (see insets of Figures 1 and 2) are divided by the corresponding values of E_P and τ_Δ and normalized to the respective ratio at [TME] = 0. The resulting data of $Q_{\Delta,r}^{TL}$, which are listed in Table 1, undoubtedly demonstrate that the quantum yield of $O_2(^1\Delta_g)$ sensitization remains constant up to [TME] = 0.12 M. Consequently, the highly reactive exciplex ($S_0{\cdot\cdot}{}^1\Delta$), which should explain the finding $Q_\Delta^{SP} > Q_\Delta^{TL}$, does not exist.

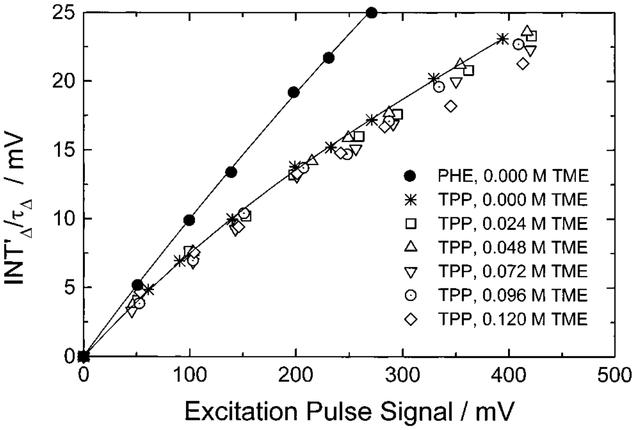

Figure 4. Dependence of the ratio of the integrated $O_2(^1\Delta_g)$ luminescence signal over the $O_2(^1\Delta_g)$ lifetime on the energy of the excitation pulse. Solid curves are third-order polynomial fits for [TME] = 0. PHE: $A_0 = 3.871 \times 10^{-5}$, $A_1 = 1.046 \times 10^{-4}$, $A_2 = -5.266 \times 10^{-8}$, $A_3 = 3.530 \times 10^{-11}$. TPP: $A_0 = 1.178 \times 10^{-6}$, $A_1 = 8.340 \times 10^{-5}$, $A_2 = -9.328 \times 10^{-8}$, $A_3 = 7.720 \times 10^{-11}$.

TABLE 1: Relative Quantum Yields $Q_{\Delta,r}TL$ of $O_2(^1\Delta_g)$ Sensitization by TPP in Air-Saturated Benzene as a Function of [TME]

	$Q_{\Delta,r}TL$		
[TME], M	1. series	2. series	average
0	1	1	1
0.024	1.10	1.00	1.05
0.048	0.99	0.99	0.99
0.072	1.01	0.92	0.97
0.096	0.93	0.94	0.94
0.120	0.95	1.01	0.98

Thus, the questions still remain, why do TL experiments apparently lead to distinctly smaller quantum yields, and which are the actual values of Q_Δ and S_Δ? We performed all these experiments under variation of the excitation pulse energy. Hereby we found that plots of $\mathrm{INT}'_\Delta/\tau_\Delta$ versus E_P more strongly deviate from linearity for the sensitizer TPP than for the reference sensitizer PHE. This is illustrated in Figure 4.

The data for TPP and PHE both determined in the absence of TME have been fitted by third degree polynomials. The corresponding fits are drawn in Figure 4 as solid curves. It is obvious that the data level off from linearity already in the low-energy range for TPP. In such a case rather accurate determination of Q_Δ^{TL} can be performed, if the coefficients A_1 of the linearly energy dependent terms of TPP ($A_1 = 8.340 \times 10^{-5}$) and PHE ($A_1 = 1.046 \times 10^{-4}$) are used for evaluation. Since the data of PHE and TPP have been determined under identical optical and instrumental conditions, $Q_\Delta^{TL}(\mathrm{TPP}) = A_1(\mathrm{TPP})Q_\Delta(\mathrm{PHE})/A_1(\mathrm{PHE})$ holds true. With $Q_\Delta(\mathrm{PHE}) = 0.98 \pm 0.05$ determined previously in air-saturated benzene by several different methods,[37] we obtain from the present luminescence measurements $Q_\Delta^{TL}(\mathrm{TPP}) = 0.78 \pm 0.04$ in almost perfect agreement with $Q_\Delta^{SP} = 0.80$. Obviously, no discrepancy exists between the results obtained with both different methods, if careful measurements of the energy dependence of the luminescence signals are performed in the low excitation energy region. Possibly, it is the very early deviation of the $O_2(^1\Delta_g)$ signals from linearity with excitation energy, which easily can be overlooked, that leads to apparently lower values of Q_Δ for TPP in time-resolved luminescence measurements.[1,3] With the value of $Q_T = 0.78$ (air-saturated) we finally determine the efficiency of singlet oxygen formation in the quenching of the TPP triplet state by O_2 in benzene as $S_\Delta = 1.0$. The present results lead us to the recommendation to use for the Zn and Mg complexes of TPP in benzene the values of Q_Δ determined by the SP method, i.e., 0.81 and 0.78 (air-saturated) and 0.84 and 0.85 (O_2-saturated), respectively.[4]

Conclusions

The speculation that in benzene an exciplex of TPP and $O_2(^1\Delta_g)$, being highly reactive toward TME, would be reponsible for the apparently smaller quantum yields of $O_2(^1\Delta_g)$ sensitization by TPP determined by time-resolved luminescence compared with stationary photochemical measurements has been disproven. No discrepancy exists between the results obtained with both different methods, if careful measurements are performed with rather high accuracy. It has been shown that quantitative time-resolved measurements of singlet oxygen are possible under conditions of very strong quenching, reducing the lifetime of $O_2(^1\Delta_g)$ to about 200 ns.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

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