

On the Effect of 1,4-Diazabicyclo[2.2.2]octane on the Singlet-Oxygen Dimol Emission: Photosensitized Generation of (¹O₂)₂

Dmitri V. Kazakov^{*,†} and Reinhard Schmidt^{*,‡}

Institute of Organic Chemistry, Ufa Scientific Center of the RAS, 71 Prospect Oktyabrya, 450054 Ufa, Russia, and Johann Wolfgang Goethe-Universität Frankfurt am Main, Institut für Physikalische und Theoretische Chemie, Max-von-Laue-Strasse 7, D-60438 Frankfurt am Main, Germany

Received: January 25, 2007; In Final Form: March 13, 2007

Time-resolved singlet-oxygen dimol luminescence has been recorded upon laser-pulsed photosensitization of singlet oxygen by 2-acetonaphthone or 1-H-phenalen-1-one in perfluorobenzene, perdeuterobenzene, and perdeuteroacetonitrile. It is shown that 1,4-diazabicyclo[2.2.2]octane (DABCO) does not enhance radiative properties of the dimol species generated by the photosensitization. Instead, DABCO strongly reduces the singlet-oxygen dimol luminescence. Rate constants for the quenching of the dimol luminescence by DABCO have been determined for the three solvents used.

Introduction

Molecular singlet oxygen in its lowest excited ¹Δ_g state (¹O₂) attracts remarkable attention because of its important role in numerous branches of science such as chemistry, biochemistry, medicine, and environment.^{1–30} One of the most interesting features of ¹O₂ is the luminescence from dimol associates (¹O₂)₂ found in the 1960s.^{31–38} However, in contrast to the rather well explored ¹O₂, the properties of (¹O₂)₂ are still poorly understood. The investigation of (¹O₂)₂ is a very difficult challenge because of its extremely short lifetime, its small radiative rate constant, and its very low stationary concentration.^{39–50} Up to now, the only way to get any information on singlet-oxygen dimol is the study of its characteristic emission in the red spectral range with principal emission bands at 634 and 703 nm, if its precursor ¹O₂ is produced in high concentration either chemically (chemiluminescence, CL)^{1,17,31–38,51–57} or by photosensitization.^{40–50}

One of the enigmas associated with singlet-oxygen dimol is the effect of 1,4-diazabicyclo[2.2.2]octane (DABCO) on the (¹O₂)₂ CL: DABCO has been reported to enhance CL, generated by the decomposition of disodium 3,3'-(1,4-naphthylidene)-dipropionate endoperoxide⁵¹ or by the reaction of hydrogen peroxide with hypochlorite ion.^{58–60} This phenomenon conflicts with the known properties of singlet oxygen, since DABCO strongly shortens the lifetime of ¹O₂,^{4,16,61} the direct precursor of (¹O₂)₂. This contradictory issue was recently addressed in a separate paper on the action of DABCO on the singlet-oxygen dimol CL generated in several peroxide reactions.⁵⁷ To complement our extensive CL study by photoluminescence measurements, we report herein on the luminescence of (¹O₂)₂ generated by photosensitization and on the influence of DABCO on this emission.

Experimental Methods

1-H-Phenalen-1-one (PH, Aldrich >97%) was purified by column chromatography with silica gel/dichloromethane.⁶²

* E-mail: chemlum@ufanet.ru (D.V.K.); R.Schmidt@chemie.uni-frankfurt.de (R. S.).

[†] Ufa Scientific Center of the RAS.

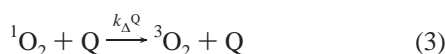
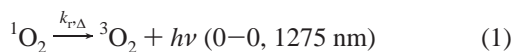
[‡] Johann Wolfgang Goethe-Universität Frankfurt am Main.

2-Acetonaphthone (AC, Aldrich, 99%) was recrystallized from 5:1 methanol/hexane. The solvents (CD₃CN, Deutero GmbH, 99%; C₆D₆, Deutero GmbH, 99%; C₆F₆, Aldrich, 99%) were used as received. Tetramethylethylene (TME, Fluka, 99%) was employed without further purification. 1,4-Diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%) was recrystallized from water.

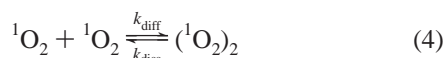
The principal setup for the time-resolved singlet-oxygen measurements has been described.⁶³ High-energy pulses (up to 30 mJ) of a frequency-tripled Nd:YAG laser (Brilliant) from Quantel (355 nm, 4 ns) have been used for excitation. The sample housing allowed the simultaneous observation of both the ¹O₂ and the (¹O₂)₂ emissions, which were focused through suited filters on a R1464 photomultiplier (Hamamatsu, sensitive below 840 nm) and a fast liquid-N₂ cooled germanium diode (North Coast EO 817P), respectively. ¹O₂ was produced exciting either PH or AC in oxygen-saturated solution in 1 cm fluorescence cells at about 23 °C. High-sample absorbances of about 1.9 (AC) and 3.6 (PH) yielded the best (¹O₂)₂ luminescence signals. The experimental emission decay curves are averages over 128 individual experiments. A 1275 nm interference filter was used for isolation of the ¹O₂ emission, whereas a 595 nm cut-on filter combined with an interference filter with peak transmissions at 630 (for the 634 nm band) or at 700 nm (for the 703 nm band) or the 595 nm cut-on filter alone (for both bands) has been used to record the (¹O₂)₂ emission. A very fast decaying initial background signal is observed with the photomultiplier even in solutions without sensitizers. To separate the perturbing scattered light and the very fast decaying residual sensitizer fluorescence penetrating the filters from the rather slow decaying (¹O₂)₂ emission, a difference technique was used. For each solution of the sensitizer, a second sample was prepared which differs from the first only by the presence of 0.3 M TME, which quenches ¹O₂ with rate constant 3.6 × 10⁷ M⁻¹ s⁻¹ and which suppresses completely any luminescence associated with singlet oxygen.⁶⁴ Thus, the difference of the singlet-oxygen emission signals sensitized by PH or AC recorded at λ > 595 nm without and with TME corresponds to the net singlet-oxygen dimol signal. This approach has been used in all experiments described below.

Results and Discussion

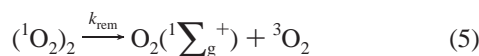
After laser-pulse excitation of a sensitizer of sufficient triplet energy like AC or PH, $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ are competitively formed with high efficiency by energy transfer if $O_2(^3\Sigma_g^-)$ ground-state oxygen (3O_2) is present. The upper excited $O_2(^1\Sigma_g^+)$ is quantitatively converted to $O_2(^1\Delta_g)$ in much less than 100 ns by electronic-to-vibrational (e-v) energy transfer to the solvents investigated.⁶⁵ Thus, the maximum concentration of 1O_2 is reached after about 300 ns in oxygenated solutions. The decay of 1O_2 occurs by phosphorescence with extremely small and solvent-dependent rate constant $k_{r,\Delta}$ and is radiationless by e-v deactivation to the solvent (k_Δ) or by deactivation by an added quencher Q ($k_{\Delta Q}$),⁴ see eqs 1–3.



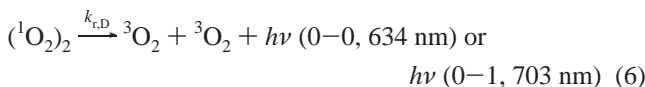
The formation of singlet-oxygen dimol occurs in the very fast equilibrium reaction of eq 4.



The rate constant of the forward reaction is assumed to be diffusion-controlled and was calculated to $k_{diff} = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in CS_2 .^{45,50} As upper limit of the backward dissociation, rate constant $k_{diss} = 3.3 \times 10^{11} \text{ s}^{-1}$ was estimated for CS_2 on the basis of diffusion control,⁴⁵ whereas $k_{diss} = 2.6 \times 10^{10} \text{ s}^{-1}$ has been determined experimentally in CCl_4 as a lower limit.^{48,50} The forward dissociation reaction of $(^1O_2)_2$ is by orders of magnitude slower and leads in CS_2 to the formation of $O_2(^1\Sigma_g^+)$ and 3O_2 , eq 5. The rate constant of this spin-forbidden removal of $(^1O_2)_2$ was determined to $k_{rem} = 1.0 \times 10^7 \text{ s}^{-1}$.⁴⁵



The last deactivation process of $(^1O_2)_2$ to be considered is radiative deactivation leading in CCl_4 with rate constant $k_{r,D} = 1.2 \times 10^3 \text{ s}^{-1}$ to two ground-state oxygen molecules and the emission of a 634 or 703 nm photon, depending on whether or not one of the 3O_2 is formed in the $\nu = 1$ vibrational excited state, see eq 6.⁴⁹



Principally, the $O_2(^1\Sigma_g^+)$ formed in the deactivation eq 5 could contribute via its very weak 765 nm emission to the overall luminescence signal if the 595 nm cut-on filter is used alone without further interference filters because then the entire 595–840 nm spectral range is monitored by the photomultiplier. However, the efficiency $k_{rem}/(k_{rem} + k_{diss}) = 3 \times 10^{-5}$ of eq 5 is extremely small; the lifetime of $O_2(^1\Sigma_g^+)$ is very short with values of 13 ns (C_6F_6), 0.6 ns (CD_3CN), and 0.3 ns (C_6D_6) estimated from quenching rate constants;⁶⁶ and the radiative rate constant of the 765 nm emission of $O_2(^1\Sigma_g^+)$ is with 1 s^{-1} really

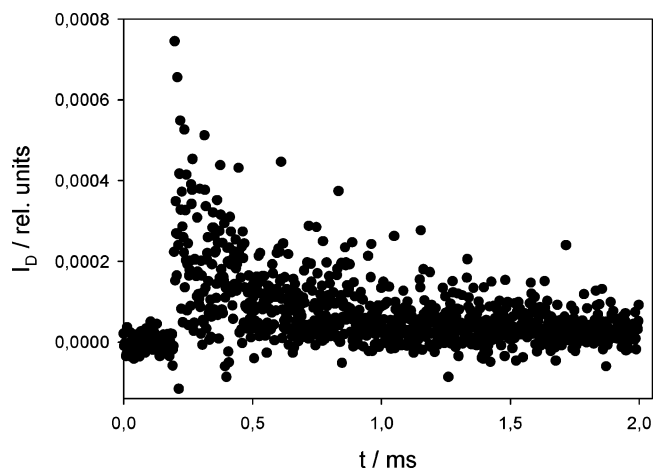


Figure 1. Decay of singlet-oxygen dimol luminescence observed through a 595 nm cut-on filter and a 630 nm interference filter sensitized by PH in C_6F_6 .

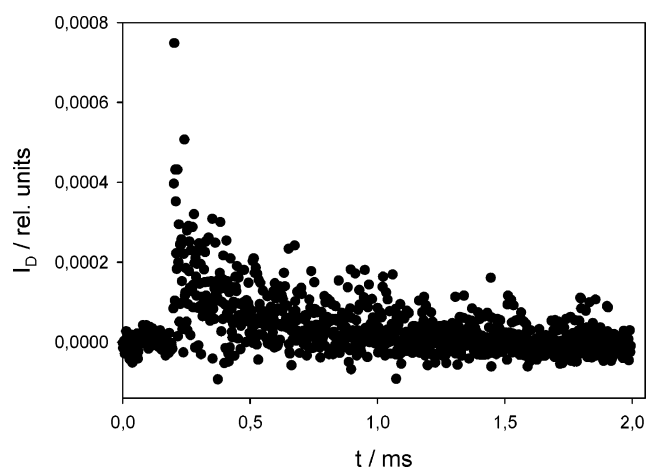


Figure 2. Decay of singlet-oxygen dimol luminescence observed through a 595 nm cut-on filter and a 700 nm interference filter sensitized by PH in C_6F_6 .

tiny,^{48,67} making the possible contribution of the $O_2(^1\Sigma_g)$ luminescence to the dimol emission negligibly weak.

We excited oxygenated solutions of PH at 355 nm in C_6F_6 and recorded under identical experimental conditions the luminescence signals described in eq 6 through either the combinations of a 595 nm cut-on filter with an interference filter with peak transmission wavelength at 630 (Figure 1) or at 700 nm (Figure 2) or the 595 nm cut-on filter alone (Figure 3). The signals of Figures 1 and 2 are very strongly scattered because of the weakness of emission and the small transmission of the filter combinations used. A significantly better signal-to-noise ratio is observed with the cut-on filter alone, see Figure 3. The general form of the decay curves, however, remains the same. Analogous results have been obtained with the other two oxygenated solvents and with the second sensitizer. The investigation of the quenching of the dimol luminescence requires signals with an acceptable signal-to-noise ratio. That is the reason why we used for the isolation of the $(^1O_2)_2$ emission in the further experiments only the cut-on filter.

In the absence of photochemically formed transient quenchers of 1O_2 , its decay should occur monoexponentially. The corresponding luminescence signal I_Δ is then given by eq 7.

$$I_\Delta = c_\Delta k_{r,\Delta} [^1O_2]_0 \exp(-t/\tau_\Delta) \quad (7)$$

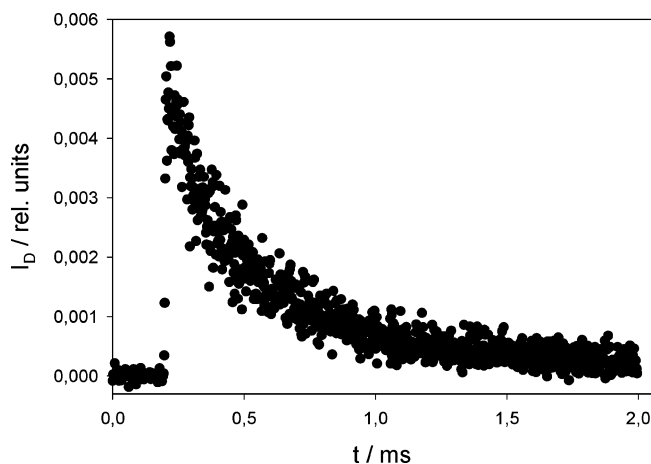


Figure 3. Decay of singlet-oxygen dimol luminescence observed through a 595 nm cut-on filter sensitized by PH in C_6F_6 .

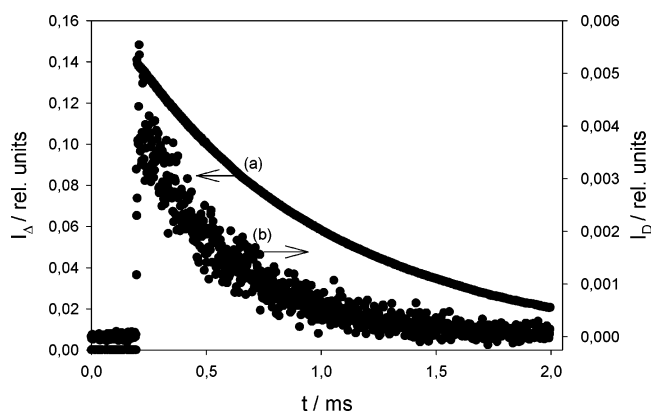


Figure 4. Decay of photosensitized 1O_2 and $(^1O_2)_2$ luminescence signals I_A (curve a) and I_D (curve b). Sensitizer: PH in CD_3CN .

where c_Δ , $[^1O_2]_0$, and τ_D are the apparatus constant, the initial concentration, and the lifetime of 1O_2 . The dimol luminescence signal I_D is given by eq 8

$$I_D = c_D k_{r,D} [(^1O_2)_2] \quad (8)$$

$[(^1O_2)_2] = K [^1O_2]^2$ holds true because of the very fast eq 4 with equilibrium constant $K = (k_{diff}/k_{diss})$ leading to eq 9 for the $(^1O_2)_2$ luminescence decay.

$$I_D = c_D k_{r,D} K [^1O_2]_0^2 \exp(-2 \times t/\tau_\Delta) \quad (9)$$

Thus, the $(^1O_2)_2$ luminescence decay time τ_{dec} should be just half the value of τ_Δ . We have found that this is valid with both sensitizers in C_6F_6 , C_6D_6 , and CD_3CN . Figures 4 and 5 illustrate the dependence of the photosensitized $(^1O_2)_2$ and 1O_2 singlet-oxygen luminescences on time in linear and semilogarithmic representations. Figure 5 with its twofold narrower scaling of $\ln(I_D)$ compared with $\ln(I_A)$ reveals particularly well the relation $\tau_{dec} = \tau_\Delta/2$ by means of the approximate parallels. The lifetime ratio $\tau_\Delta/\tau_{dec} = 2.1$ is calculated from the slopes of both linear fits. The deviation of $\tau_\Delta = 0.94$ ms in the experiment of Figures 4 and 5 from $\tau_\Delta = 1.5$ ms in pure CD_3CN ⁶⁸ is caused by quenching of 1O_2 by the sensitizer.

Equations 7 and 9 lead to eq 10 which demands a linear correlation of $\log(I_D)$ with $\log(I_A)$ with slope 2.

$$\log(I_D) = \log(\{c_D k_{r,D} K\} / \{c_\Delta k_{r,\Delta}\}^2) + 2 \times \log(I_A) \quad (10)$$

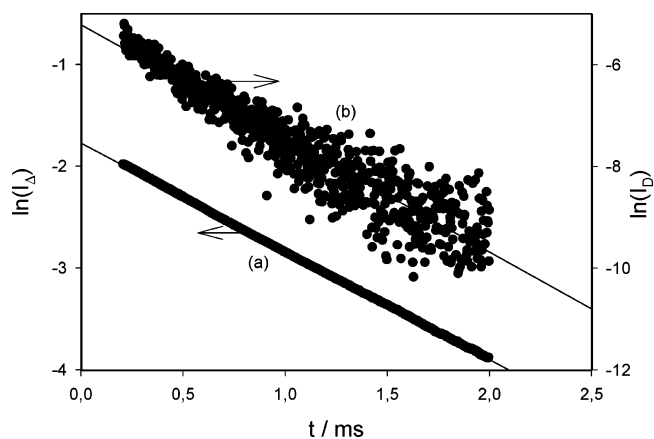


Figure 5. Semilogarithmic plot of photosensitized 1O_2 and $(^1O_2)_2$ luminescence signals I_A (curve a) and I_D (curve b) indicating first-order decay. Sensitizer: PH in CD_3CN .

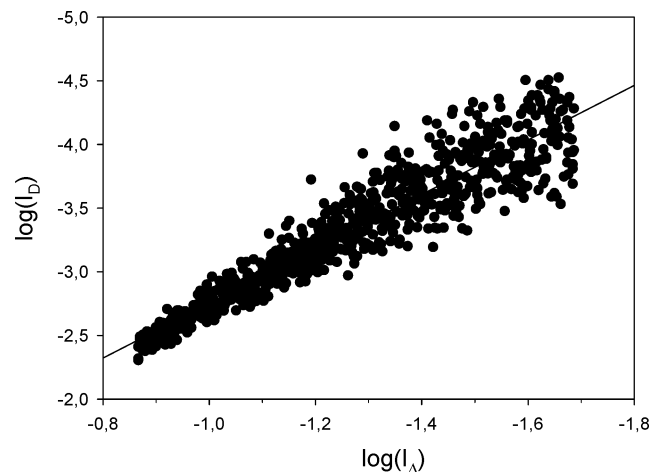


Figure 6. Double-logarithmic plot of $(^1O_2)_2$ signal I_D versus 1O_2 signal I_A . Sensitizer: PH in CD_3CN .

Figure 6 illustrates the experiment of Figures 4 and 5 according to eq 10. The double-logarithmic representation yields actually a rather nice linear correlation with a slope of 2.14 in agreement with the square dependence of I_D on I_A resulting from the fast equilibrium 4.

Analogous dependences have been obtained in C_6F_6 , and C_6D_6 . However, Figures 4–6 describe one of the best experiments performed. In most of the other runs, the slope of the double-logarithmic plot lies in the range 1.9–2.5 with lower correlation coefficients. The deviation from 2 is, obviously, associated with the high scatter of the $(^1O_2)_2$ emission which, unfortunately, brings a significant experimental error.

Additionally, deviation from the linearity of the semilogarithmic plots in the beginning of the decay of 1O_2 and $(^1O_2)_2$ is observed in many runs. This is illustrated by Figures 7–9. The initial deviation of the luminescence decay from monoexponential behavior is explained by the photochemical production of short-lived quenchers of 1O_2 which itself decays already during τ_Δ . Such effects are regularly observed if sensitizers are excited with pulses of high energy in solvents of rather long singlet-oxygen lifetimes.^{4,69}

The double-logarithmic representation of Figure 9 is almost linear although a significant deviation from linearity is observed for the same experiment in the time-dependent representations of Figure 8. This indicates that the square dependence of I_D on I_A holds also true for more complex and faster deactivation in complete accordance with the very fast equilibrium 4.

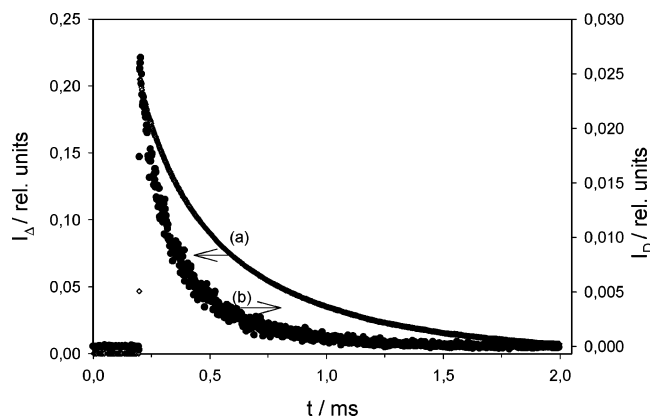


Figure 7. Decay of photosensitized $^1\text{O}_2$ and $(^1\text{O}_2)_2$ luminescence signals I_Δ (curve a) and I_D (curve b). Sensitizer AC in CD_3CN .

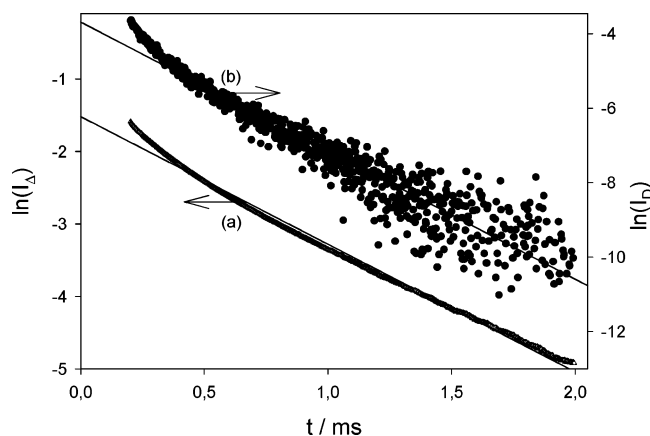


Figure 8. Semilogarithmic plot of $^1\text{O}_2$ and $(^1\text{O}_2)_2$ luminescence signals I_Δ (curve a) and I_D (curve b) indicating the initial deviation from first-order decay. Sensitizer AC in CD_3CN . The lifetime ratio $\tau_\Delta/\tau_{\text{dec}} = 1.96$ is calculated from the slopes of both linear fits.

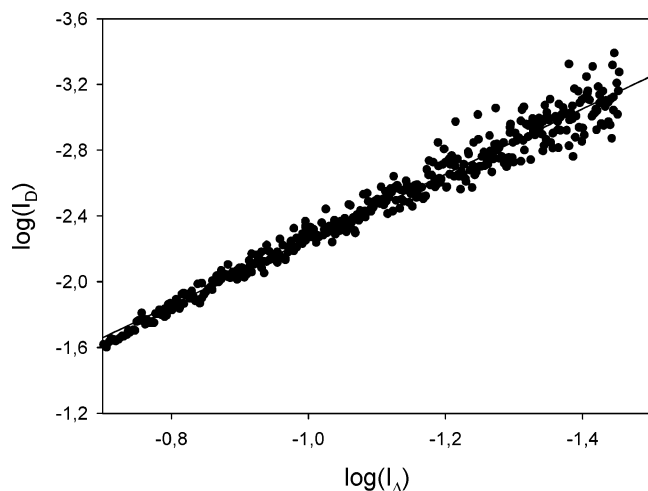


Figure 9. Double-logarithmic plot of $(^1\text{O}_2)_2$ signal I_D versus $^1\text{O}_2$ signal I_Δ . Sensitizer: AC in CD_3CN . The slope of the fit is 1.99.

An acceleration of the decay is caused upon addition of a quencher of $^1\text{O}_2$. Because $^1\text{O}_2$ is the precursor of $(^1\text{O}_2)_2$, the luminescence of the latter should also be diminished and that is indeed the case. The decay time τ_{dec} of the $(^1\text{O}_2)_2$ luminescence sensitized either by AC or PH in CD_3CN , C_6F_6 , and C_6D_6 is efficiently reduced by addition of TME. Moreover, the ratio $\tau_\Delta/\tau_{\text{dec}}$ remains constant between 2.0 and 2.3 under a wide range of TME concentrations (up to 1×10^{-3} M) in CD_3CN reducing τ_Δ down to about 30 μs .

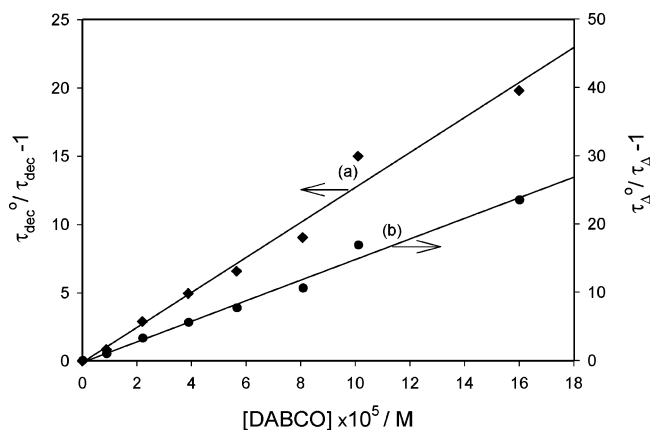


Figure 10. Stern–Volmer dependence of the quenching of the $(^1\text{O}_2)_2$ (line a) and $^1\text{O}_2$ (line b) emissions by DABCO. Sensitizer AC in C_6D_6 . Note the different scaling of the $\tau_{\text{dec}}^0/\tau_{\text{dec}} - 1$ and $\tau_\Delta^0/\tau_\Delta - 1$ axis.

TABLE 1: Stern–Volmer Constants $K_{\text{SV},D} = \tau_{\text{dec}}^0 k_D^Q$ and $K_{\text{SV},\Delta} = \tau_\Delta^0 k_\Delta^Q$ of $(^1\text{O}_2)_2$ and $^1\text{O}_2$ Emission Quenching by DABCO, Respectively

sensitizer	solvent					
	C_6D_6		C_6F_6		CD_3CN	
	$\tau_{\text{dec}}^0/\mu\text{s}$	$K_{\text{SV},D}/\text{M}^{-1}$	$\tau_{\text{dec}}^0/\mu\text{s}$	$K_{\text{SV},D}/\text{M}^{-1}$	$\tau_{\text{dec}}^0/\mu\text{s}$	$K_{\text{SV},D}/\text{M}^{-1}$
PH	240	1.4×10^5	790	2.7×10^4	350	1.60×10^5
AC	250	1.3×10^5	460	2.6×10^4	200	2.80×10^5

sensitizer	solvent					
	C_6D_6		C_6F_6		CD_3CN	
	$\tau_\Delta^0/\mu\text{s}$	$K_{\text{SV},\Delta}/\text{M}^{-1}$	$\tau_\Delta^0/\mu\text{s}$	$K_{\text{SV},\Delta}/\text{M}^{-1}$	$\tau_\Delta^0/\mu\text{s}$	$K_{\text{SV},\Delta}/\text{M}^{-1}$
PH	550	1.5×10^5	2320	4.3×10^4	820	3.4×10^5
AC	555	1.5×10^5	1280	3.6×10^4	560	2.2×10^5

Thus, it is proven that the luminescence recorded at $\lambda > 595$ nm in these photosensitization experiments is caused by the emission from singlet-oxygen dimol species. Thus, we were able to test the controversial influence of DABCO on the $(^1\text{O}_2)_2$ luminescence. In the absence of added quencher Q, when deactivation of $^1\text{O}_2$ occurs principally by the solvent, $\tau_\Delta^0 = 1/k_\Delta$ holds true. In the presence of Q, the lifetime of $^1\text{O}_2$ is given by eq 11.

$$\tau_\Delta = (k_\Delta + k_\Delta^Q [\text{Q}])^{-1} \quad (11)$$

If experiments are performed without and with quencher, the ratio $\tau_\Delta^0/\tau_\Delta$ is given by the Stern–Volmer eq 12.

$$\tau_\Delta^0/\tau_\Delta = 1 + \tau_\Delta^0 k_\Delta^Q [\text{Q}] \quad (12)$$

Analogous treatment of the $(^1\text{O}_2)_2$ luminescence leads with k_D^Q , the rate constant of $(^1\text{O}_2)_2$ emission quenching, to eq 13.

$$\tau_{\text{dec}}^0/\tau_{\text{dec}} = 1 + \tau_{\text{dec}}^0 k_D^Q [\text{Q}] \quad (13)$$

We found that the decay times of the $(^1\text{O}_2)_2$ emission are strongly reduced by DABCO. The quenching follows the Stern–Volmer eq 13. The straight line (a) of Figure 10 represents the linear least-squares fit of $\tau_{\text{dec}}^0/\tau_{\text{dec}} - 1$ to $[\text{DABCO}]$ in C_6D_6 and yields as slope the Stern–Volmer constant $K_{\text{SV},D} = 1.3 \times 10^5 \text{ M}^{-1}$. Analogous linear dependences have been obtained in CD_3CN and C_6F_6 using both sensitizers PH and AC. Table 1 lists the Stern–Volmer constants $K_{\text{SV},D}$.

For comparison, we have also investigated the quenching of $^1\text{O}_2$ by DABCO. Again, a Stern–Volmer behavior was found, see the fitted straight line (b) of Figure 10 which results in the

TABLE 2: Rate Constant k_D^Q and k_A^Q of $(^1O_2)_2$ and 1O_2 Emission Quenching by DABCO, Respectively

sensitizer	C_6D_6 $k_D^Q/M^{-1} s^{-1}$	C_6F_6 $k_D^Q/M^{-1} s^{-1}$	CD_3CN $k_D^Q/M^{-1} s^{-1}$
PH	5.6×10^8	3.4×10^7	4.6×10^8
AC	5.1×10^8	5.7×10^7	14×10^8
average	5.4×10^8	4.5×10^7	9.3×10^8

sensitizer	C_6D_6 $k_A^Q/M^{-1} s^{-1}$	C_6F_6 $k_A^Q/M^{-1} s^{-1}$	CD_3CN $k_A^Q/M^{-1} s^{-1}$
PH	2.8×10^8	1.9×10^7	4.1×10^8
AC	2.7×10^8	2.8×10^7	3.9×10^8
average	2.7×10^8	2.3×10^7	4.0×10^8

Stern–Volmer constant $K_{SV,\Delta} = 1.5 \times 10^5 M^{-1}$. The values of $K_{SV,\Delta}$ are also collected in Table 1. Inspection reveals that in a given solvent the Stern–Volmer constants $K_{SV,D}$ and $K_{SV,\Delta}$ are independent of the sensitizer used. Table 1 also lists the lifetimes τ_{dec}^0 and τ_{Δ}^0 determined in the DABCO-free solutions. Dividing the Stern–Volmer constants by the corresponding lifetimes yields the quenching rate constants k_D^Q and k_A^Q of the $(^1O_2)_2$ and 1O_2 emissions by DABCO given in Table 2. The average values of the rate constant k_A^Q of Table 2 of 2.7×10^8 (C_6D_6) and $4.0 \times 10^8 M^{-1} s^{-1}$ (CD_3CN) agree very well with reliable literature data of $(2.5–2.9) \times 10^8$ (C_6H_6) and $(4.0–4.9) \times 10^8 M^{-1} s^{-1}$ (CH_3CN) determined in the corresponding nondeuterated solvents.^{16,70–74} The average value $k_A^Q = 2.3 \times 10^7 M^{-1} s^{-1}$ in the nonpolar C_6F_6 is 1 order of magnitude smaller but is similar to $k_A^Q = 4.4 \times 10^7 M^{-1} s^{-1}$ in CCl_4 .⁵⁷

Table 2 reveals that, despite the scatter of the individual k_D^Q data in CD_3CN , the average rate constants of $(^1O_2)_2$ emission quenching are in all three solvents twofold larger than the average numbers of k_A^Q . This result is only on first sight surprising, as the deactivation of $(^1O_2)_2$ is strongly coupled to the deactivation of 1O_2 via the fast equilibrium eq 4. The actual lifetime τ_D of a single $(^1O_2)_2$ complex is entirely determined by the rate constant k_{diss} of its backward dissociation, which is with $k_{diss} = 3.3 \times 10^{11} s^{-1}$ (CS_2) and $= 2.6 \times 10^{10} s^{-1}$ (CCl_4) by orders of magnitude faster than other deactivation processes of eqs 4–6. Thus, τ_D ranges between about 3 and 40 ps.^{45,48,50} Because of this very short lifetime, any bimolecular quenching event will be extremely inefficient. Therefore, the bimolecular quenching of 1O_2 affects indirectly the decay time τ_{dec} of the $(^1O_2)_2$ emission via eq 4. Since $\tau_{dec} = \tau_{\Delta}/2$, we obtain $\tau_{dec}^0 = \tau_{\Delta}^0/2$ and $\tau_{dec} = 0.5 \times (k_{\Delta} + k_A^Q [Q])^{-1}$ and finally the Stern–Volmer eq 14.

$$\tau_{dec}^0/\tau_{dec} = 1 + \tau_{dec}^0 \times 2 \times k_A^Q [Q] \quad (14)$$

The comparison of eqs 13 and 14 demonstrates that $k_D^Q = 2 \times k_A^Q$ is actually expected as long as the forward and backward reactions of the equilibrium 4 are much faster than the single overall deactivation processes of $(^1O_2)_2$ and 1O_2 . Consequently, k_D^Q does not have the meaning of a bimolecular quenching rate constant of $(^1O_2)_2$. Instead, it represents twice the bimolecular quenching rate constant of 1O_2 .

To check whether in our quenching experiments, in which solvent, sensitizer concentration, and excitation pulse energy have been kept constant and only [DABCO] was changed, an increase of the radiative probability of the dimol species took place, we carefully analyzed the double-logarithmic correlations according to eq 10. Since under these conditions the quantities c_D , c_{Δ} , K , and $k_{r,\Delta}$ of the intercept $\log\{c_D k_{r,D} K / \{c_{\Delta} k_{r,\Delta}\}^2\}$ are constant, an increase of the intercept with [DABCO] should indicate a bimolecular collision-induced enhancement of the $(^1O_2)_2$ radiation probability. However, no significant changes

of the intercept have been observed in the quenching experiments with AC and PH in the three different solvents investigated.

Conclusions

DABCO does not enhance radiative properties of the singlet-oxygen dimol species in perfluorobenzene, deuterobenzene, or deuterioacetonitrile but strongly reduces its luminescence decay time because of the quenching of 1O_2 . Thus, this photoluminescence study confirms the results of our previous investigation of the effect of DABCO on the emission of singlet-oxygen dimol generated in different chemical peroxide reactions, which showed that DABCO quenches the chemiluminescence of $(^1O_2)_2$.⁵⁷

Acknowledgment. The research in Ufa was supported by the Russian Foundation for Basic Research (grant No 05-03-32663a), the Leading Scientific School Support Program (grant No 5486.2006.3), and the Branch of Chemistry and Material Sciences of the RAS (No1-OKh). D. V. K. is grateful to the INTAS for YS fellowship (2005–2007, ref number 04-83-3280). R. S. thanks the Adolf-Messer-Stiftung for financial support.

References and Notes

- (1) Adam, W.; Kazakov, D. V.; Kazakov, V. P. *Chem. Rev.* **2005**, *105*, 3371.
- (2) Krasnovsky, A. A., Jr. *Biophysics* **2004**, *49*, 289.
- (3) Aubry, J.–M.; Pierlot, C.; Rigaudy, J.; Schmidt, R. *Acc. Chem. Res.* **2003**, *36*, 668.
- (4) Schweitzer, C.; Schmidt, R. *Chem. Rev.* **2003**, *103*, 1685.
- (5) Weldon, D.; Poulsen, T. D.; Mikkelsen, K. V.; Ogilby, P. R. *Photochem. Photobiol.* **1999**, *70*, 369.
- (6) Gorman, A. A.; Rodgers, M. A. *Photochem. Photobiol. B: Biol.* **1992**, *14*, 159.
- (7) Briviba, K.; Sies, H. *Methods Enzymol.* **2000**, *319*, 222.
- (8) Krasnovsky, A. A., Jr. *Membr. Cell Biol.* **1998**, *12*, 665.
- (9) Adam, W.; Prein, M. *Acc. Chem. Res.* **1996**, *29*, 275.
- (10) Adam, W.; Wirth, T. *Acc. Chem. Res.* **1999**, *32*, 703.
- (11) Clennan, E. L. *Tetrahedron* **2000**, *56*, 9151.
- (12) Foote, C. S.; Clennan, E. L. In *Active Oxygen in Chemistry*; Foote, C. S., Valentine, J. S., Greenberg, A., Liebman, J. F., Eds.; Chapman and Hall: London, 1995; Vol. 2, p 105.
- (13) DeRosa, M. C.; Crutchley, R. J. *Coord. Chem. Rev.* **2002**, *233*, 351.
- (14) Redmond, R. W.; Gamlin, J. N. *Photochem. Photobiol.* **1999**, *70*, 391.
- (15) Wilkinson, F. *Pure Appl. Chem.* **1997**, *69*, 851.
- (16) Wilkinson, F.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 663; <http://www.rcdc.nd.edu/compilations/SingOx/table8/t8.htm>.
- (17) Khan, A. U. *Int. J. Quantum. Chem.* **1991**, *39*, 251.
- (18) In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC: Boca Raton, FL, 1985.
- (19) In *Organic Chemistry: Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Vol. 40.
- (20) *Singlet Oxygen, Reactions with Organic Compounds and Polymers*; Ranby, B., Rabeck, J. F., Eds.; Wiley: New York, 1978.
- (21) *Singlet Molecular Oxygen*; Schaap, A. P., Ed.; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1976.
- (22) Paterson, M. J.; Christiansen, O.; Jensen, F.; Ogilby, P. R. *Photochem. Photobiol.* **2006**, *82*, 1136.
- (23) Schmidt, R. *Photochem. Photobiol.* **2006**, *82*, 1161.
- (24) Redmond, R. W.; Kochevar, I. E. *Photochem. Photobiol.* **2006**, *82*, 1178.
- (25) Skovsen, E.; Snyder, J. W.; Ogilby, P. R. *Photochem. Photobiol.* **2006**, *82*, 1187.
- (26) Jarvi, M. T.; Niedre, M. J.; Patterson, M. S.; Wilson, B. C. *Photochem. Photobiol.* **2006**, *82*, 1198.
- (27) Hideg, É.; Kálai, T.; Kós, P. B.; Asada, K.; Hideg, K. *Photochem. Photobiol.* **2006**, *82*, 1211.
- (28) Cadet, J.; Ravanat, J.–L.; Martinez, G. R.; Medeiros M. H. G.; Di Mascio, P. *Photochem. Photobiol.* **2006**, *82*, 1219.
- (29) Clennan, E. L.; Zhang, D.; Singleton, J. *Photochem. Photobiol.* **2006**, *82*, 1226.

- (30) Griesbeck, A. G.; Bartoschek, A.; Neudörfl, J.; Miara, C. *Photochem. Photobiol.* **2006**, *82*, 1233.
- (31) Seliger, H. H. *Anal. Biochem.* **1960**, *1*, 60.
- (32) Stauff, J.; Schmidkunz, H. *Z. Phys. Chem. (Frankfurt)*, **1962**, *35*, 295.
- (33) Khan, A. U.; Kasha, M. *J. Chem. Phys.* **1963**, *39*, 2105.
- (34) Khan, A. U.; Kasha, M. *Nature* **1964**, *204*, 241.
- (35) Browne, R. J.; Ogryzlo, E. A. *Proc. Chem. Soc. London* **1964**, 117.
- (36) Arnold, S. J.; Ogryzlo, E. A.; Witzke, H. *J. Chem. Phys.* **1964**, *40*, 1769.
- (37) Seliger, H. H. *J. Chem. Phys.* **1964**, *40*, 3133.
- (38) Khan, A. U.; Kasha, M. *J. Am. Chem. Soc.* **1966**, *88*, 1574.
- (39) Arnold, S. J.; Kubo, M.; Ogryzlo, E. A. *Adv. Chem. Ser.* **1968**, *77*, 133.
- (40) Krasnovsky, A. A., Jr.; Neverov, K. V. *Chem. Phys. Lett.* **1990**, *167*, 591.
- (41) Krasnovsky, A. A., Jr.; Neverov, K. V. *Biomol. Spectrosc.* **1993**, *56*.
- (42) Krasnovsky, A. A., Jr.; Neverov, K. V. *Biophysics* **1988**, *33*, 884.
- (43) Neverov, K. V.; Krasnovsky, A. A., Jr. *Opt. Spectrosc.* **1991**, *71*, 61.
- (44) Krasnovsky, A. A., Jr.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 6013.
- (45) Scurlock, R. D.; Ogilby, P. R. *J. Phys. Chem.* **1996**, *100*, 17226.
- (46) Chou, P.-T.; Wei, G.-T.; Lin, C.-H.; Wei, C.-Y.; Chang, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 3031.
- (47) Chou, P.-T.; Chen, Y.-C.; Wei, C.-Y.; Chen, S.-J.; Lu, H. L.; Lee, M. Z. *Chem. Phys. Lett.* **1997**, *280*, 134.
- (48) 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.
- (49) Chou, P.-T.; Chen, Y.-C.; Wei, C.-Y. *Chem. Phys. Lett.* **1998**, *294*, 579.
- (50) Chou, P.-T.; Chen, Y.-C.; Wei, C.-Y.; Lee, M.-Z. *J. Am. Chem. Soc.* **1998**, *120*, 4883.
- (51) Di Mascio, P.; Sies, H. *J. Am. Chem. Soc.* **1989**, *111*, 2909.
- (52) Almeida, E. A.; Miyamoto, S.; Martinez, G. R.; Medeiros, M. H. G.; Di Mascio, P. *Anal. Chim. Acta* **2003**, *482*, 99.
- (53) Miyamoto, S.; Martinez, G. R.; Medeiros, M. H. G.; Di Mascio, P. *J. Am. Chem. Soc.* **2003**, *125*, 6172.
- (54) Di Mascio, P.; Bechara, E. J. H.; Rubim, J. C. *Appl. Spectrosc.* **1992**, *46*, 236.
- (55) Fu, Y.; Krasnovsky, A. A., Jr.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 10282.
- (56) Adam, W.; Kiefer, W.; Kazakov, D. V.; Kazakov, V. P.; Latypova, R. R.; Schlücker, S. *Photochem. Photobiol. Sci.* **2004**, *3*, 182.
- (57) Kazakov, D. V.; Kazakov, V. P.; Maistrenko, G. Ya.; Mal'zev, D. V.; Schmidt, R. *J. Phys. Chem. A* **2007**, *111*, 4267.
- (58) Deneke, C. F.; Krinsky, N. I. *Photochem. Photobiol.* **1977**, *25*, 299.
- (59) Deneke, C. F.; Krinsky, N. I. *J. Am. Chem. Soc.* **1976**, *98*, 3041.
- (60) Lengfelder, E.; Cadenas, E.; Sies, H. *FEBS Lett.* **1983**, *164*, 366.
- (61) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423.
- (62) Schmidt, R.; Shafii, F.; Hild, M. *J. Phys. Chem. A* **1999**, *103*, 2599.
- (63) Schmidt, R.; Tanielian, C.; Dunsbach, R.; Wolff, C. *J. Photochem. Photobiol. A: Chem.* **1994**, *79*, 11.
- (64) Schmidt, R.; Tanielian, C. *J. Phys. Chem. A* **2000**, *104*, 3177.
- (65) Schmidt, R.; Bodesheim, M. *Chem. Phys. Lett.* **1993**, *213*, 111.
- (66) Schmidt, R.; Bodesheim, M. *J. Phys. Chem. A* **1998**, *102*, 4769.
- (67) Schmidt, R.; Bodesheim, M. *J. Phys. Chem.* **1995**, *99*, 15919.
- (68) Clough, R. L.; Dillon, M. P.; Iu, K.-K.; Ogilby, P. R. *Macromolecules* **1989**, *22*, 3620 and own unpublished results.
- (69) Schmidt, R.; Brauer, H.-D. *J. Am. Chem. Soc.* **1987**, *109*, 6976.
- (70) Iu, K.-K.; Thomas, J. K. *J. Photochem. Photobiol. A* **1993**, *71*, 55.
- (71) Gorman, A. A.; Hamblett, I.; Smith, K.; Standen, M. C. *Tetrahedron Lett.* **1984**, *25*, 581.
- (72) Shiozaki, H.; Nakazumi, H.; Takamura, Y.; Kitao, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2653.
- (73) Clennan, E. L.; Noe, L. J.; Wen, T.; Szneler, E. *J. Org. Chem.* **1989**, *54*, 3581.
- (74) Gorman, A. A.; Hamblett, I.; Smith, K.; Standen, M. C. *Tetrahedron Lett.* **1984**, *25*, 581.