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On the Effect of 1,4-Diazabicyclo[2.2.2]octane on the Singlet-Oxygen Dimol Emission: Chemical Generation of $(^1O_2)_2$ in Peroxide Reactions

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The acetone-catalyzed decomposition of monoperoxysulfate ions, the molybdate ion-induced decay of hydrogen peroxide, and the reactions of *N*-chlorosuccinimide or *N*-bromosuccinimide with hydrogen peroxide and of dimethyldioxirane with tertiary amines as well as the thermal decomposition of 1,4-dimethylnaphthalene endoperoxide lead to the chemiluminescence of singlet-oxygen dimol species $(^1O_2)_2$ emitting at 634 and 703 nm. In contrast to the expected enhancement of $(^1O_2)_2$ chemiluminescence upon addition of 1,4-diazabicyclo-[2.2.2]octane (DABCO) [Deneke, C.F.; Krinsky, N. I. *J. Am. Chem. Soc.* **1976**, *98*, 3041. Di Mascio, P.; Sies, H. *J. Am. Chem. Soc.* **1989**, *111*, 2909.], quenching has been observed. Our data show that enhancement of singlet-oxygen dimol chemiluminescence is not a general phenomenon and, consequently, DABCO is not a reliable chemiluminescent probe for the presence of $(^1O_2)_2$ in chemical and biochemical systems.

Introduction

Singlet-oxygen chemiluminescence (CL) has been spectroscopically established in the earlier 1960s in the hypochlorite/hydrogen peroxide reaction and related systems.[1−9] It was shown that the CL in the near-infrared (NIR) spectral range is caused by oxygen in its lowest excited singlet state, $O_2(^1\Delta_g)$ ($\equiv {}^1O_2$, monomol emission), whereas the emission in the visible (VIS) region with principal emission bands at 634 and 703 nm originates from its dimer $O_2(^1\Delta_g)_2$ ($\equiv (^1O_2)_2$, dimol emission). The discovery of the singlet-oxygen CL has made a sustaining impact on the development of numerous branches of $^1O_2$ chemistry. The large environmental and biomedical significance of singlet oxygen as well as its important role in organic synthesis is now well recognized.[9−27]

Although valuable information on the properties of both $^1\Delta_g$ and $^1\Sigma_g{}^+$ excited singlet states of O_2 has been acquired,[24,25] the binary excited $O_2(^1\Delta_g)_2$ complex is still a rather unknown species to date, mostly because of its extremely short lifetime. From photosensitized studies, it is known that the dimol and monomol singlet-oxygen species are in a very fast equilibrium, see Scheme 1.

SCHEME 1:

$$^1O_2 + {}^1O_2 \underset{k_\mathrm{diss}}{\overset{k_\mathrm{diff}}{\rightleftharpoons}} (^1O_2)_2 \rightarrow {}^3O_2 + {}^3O_2 + h\nu\ (634\ \mathrm{nm})\ \text{or}\ h\nu\ (703\ \mathrm{nm})$$

The formation of $(^1O_2)_2$ is assumed to occur with diffusion-controlled rate constant k_diff. The dissociation rate constant k_diss is estimated to be between 2.6×10^{10} and 3.3×10^{11} s^{-1}.[28−32] Other deactivation processes of $(^1O_2)_2$ are much slower. Consequently, its lifetime lies in the picosecond range. Radiative deactivation of $(^1O_2)_2$ leads to formation of two $O_2(^3\Sigma_g{}^-)$ ground-state molecules ($\equiv {}^3O_2$) and the emission of a 634 or 703 nm photon, depending on whether or not one of the $^3O_2$ is formed in the $v = 1$ vibrational excited state.

In spite of the rather limited information about its properties, $(^1O_2)_2$ has often been invoked to explain the origin of VIS CL in chemical and biochemical reactions with participation of singlet oxygen.[9,27] Several important questions associated with dimol CL are still left open. One of the most intriguing queries is the influence of cyclic diazocompounds on the $(^1O_2)_2$ CL in solution. Deneke and Krinsky found that the CL bands of the dimol at 634 and 703 nm of the ClO^-/H_2O_2 system increased in the presence of certain cyclic diazocompounds, in particular with 1,4-diazabicyclo[2.2.2]octane (DABCO).[33,34] These findings, which subsequently have been confirmed by Lengfelder et al.,[35] have paved a way for the use of DABCO as a test for singlet oxygen and its dimol in complex biological systems.[36−42] In this connection, this "DABCO effect" has some similarity with the increase of the 703 nm emission of $(^1O_2)_2$ in its molecular complexes with some photosensitizers observed by Krasnovsky and Neverov.[43]

Such a stimulation of the dimol emission by DABCO is very surprising since it lies in contradiction with the well-known photophysics of singlet oxygen: DABCO is known to strongly reduce the lifetime of $^1O_2$, the direct precursor of $(^1O_2)_2$ (Scheme 1).[14] As a matter of fact, Kanofsky questioned the direct emission enhancing effect of DABCO and suggested that it causes the CL increase indirectly on account of an increased rate of $^1O_2$ production.[44] However, Di Mascio and Sies subsequently showed that DABCO enhances the dimol emission at 703 nm not only in the hypochlorite/H_2O_2 system but also in the thermal decomposition of disodium 3,3′-(1,4-naphthylidene)-dipropionate endoperoxide in water.[45] Very important is their finding that neither the rate of endoperoxide decomposition nor the singlet oxygen yields of the endoperoxide and of the $ClO^-/$

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H_2O_2 system were influenced by DABCO. However, we have recently mentioned our arguments, which cause us to not regard DABCO as a reliable probe for the detection of $(^1O_2)_2$.[27]

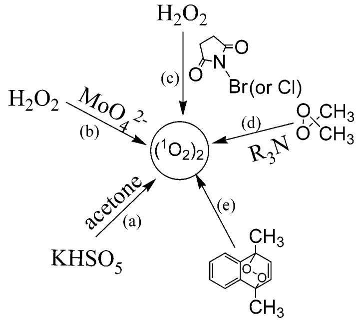
The most important question still left open in this context is whether the enhancement of the dimol CL by DABCO is a general phenomenon for all peroxide reactions with $(^1O_2)_2$ participation or whether this enhancement is only specific for aqueous media, where the effect of DABCO has been discovered. The incentive to the present work was to fill this knowledge gap. We report herein results of our extensive study on singlet-oxygen dimol CL in many peroxide reactions and on the effect of DABCO on the $(^1O_2)_2$ emission.

Experimental Methods

General Aspects. The UV absorption spectra were acquired with a Specord M-40 Carl Zeiss Jena spectrophotometer. ^1H NMR spectra were recorded on an AM 300 Bruker (300 MHz) NMR spectrometer. The setup for the time-resolved measurement of photosensitized $^1O_2$ emission has been described.[46] VIS CL was measured with the apparatus described previously using a photomultiplier sensitive between 330 and 750 nm.[47] NIR CL was recorded by means of a photomultiplier (cooled at −60 °C) sensitive up to 1350 nm. The solvents used (all of pure for analysis grade) were dried according to the literature[48] and were freshly distilled prior to use. D_2O (Aldrich, 99.9%), $CDCl_3$ (Aldrich, 99.8%), and acetone-d_6 (Aldrich, 99.9%) were taken as received. Twice-distilled water was employed in all experiments. The source of $KHSO_5$ was the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (Curox) which was used without further purification. DABCO, *N*-chlorosuccinimide (NCS), and *N*-bromosuccinimide (NBS) were twice recrystallized from water. NaN_3 (Aldrich, 99.99%) was used as received. Al_2O_3 (acid, basic, or neutral) and silica gel (surface area 600 m^2/g and particle size 0.0075, 0.125−0.169, or 0.160−0.200 mm) were heated for 3 h to 150 °C prior to use. 1,4-Dimethylnaphthalene (DMN, Aldrich, 95%) was distilled prior to use. The endoperoxide of DMN (DMNPO) was produced by sensitized photoxygenation and was purified according to published procedures.[49,50] Identification and quantification of DMNPO has been carried out by ^1H NMR spectroscopy by the characteristic methyl signal at δ 1.85 ppm in $CDCl_3$. DMNPO was supported onto silica gel and Al_2O_3 surfaces as follows: 0.1 g of silica gel or Al_2O_3 was given to 0.5 mL solution of DMNPO in CCl_4. The suspension obtained was first stirred and was later decanted. Residual solvent was removed from the powder by evaporation at low pressure. The procedures were performed keeping the temperature continuously at 0 °C. Solutions of dimethyldioxirane[51,52] in the parent liquid ketone[53,54] as well as ketone-free solutions in CCl_4[55] were prepared as described in the literature. The peroxide content of the dioxiranes was determined by iodometry.

VIS and NIR CL Measurements in Peroxide Reactions. An aliquot of a hydrogen peroxide or dimethyldioxirane solution was transferred to a cuvette, which was placed directly above an appropriate interference filter shielding the photocathode of the photomultiplier. The distance between the bottom of the cuvette and the photocathode was 30 mm and was kept constant. Subsequently, an aliquot of a solution of NCS, NBS, or Na_2MoO_4 (for H_2O_2) or of a solution of tertiary amines (for dimethyldioxirane) was rapidly (ca. 1 s) injected into the peroxide solution, and immediately CL recording was started. In the case of $KHSO_5$, an appropriate amount of Curox was transferred into the cuvette. Then, an aliquot of a buffered ($Na_2CO_3/NaHCO_3$, pH = 10) aqueous (H_2O or D_2O) acetone solution was added, and the CL was recorded. The DMNPO solution was put into the cuvette thermostated at the desired temperature, and CL recording was started immediately. Since the CL reactions were too fast and/or the emission intensities were too low to record continuous CL spectra, a point-by-point determination of the CL was carried out by means of cutoff filters. The measured VIS CL spectra were corrected for the spectral sensitivity of the photomultiplier. In separate experiments, visible CL was recorded through interference filters with transmission maxima at 575, 625, or 700 nm.

SCHEME 2: Generation of $(^1O_2)_2$ in the Peroxide Reactions Investigated



Results and Discussion

Singlet-Oxygen Dimol CL in Peroxide Reactions. The search of convenient systems for $(^1O_2)_2$ formation was the primary step of our study. Generation of $(^1O_2)_2$ was expected in the reactions with rather high yields of $^1O_2$.[27] Actually, we observed VIS CL in the peroxide reactions shown in Scheme 2: the acetone-catalyzed decomposition of $KHSO_5$ (a),[56,57] the reactions of H_2O_2 with molybdate ion (b)[58,59] and with NCS or NBS (c),[60] the tertiary amines-induced reaction of dimethyldioxirane (d),[61−63] and the thermal decomposition of DMNPO (e).[50]

Involvement of $(^1O_2)_2$ in CL has been proved by (1) the careful spectral analysis of the VIS emission to reveal the characteristic bands of $(^1O_2)_2$ at 634 and 703 nm, (2) the investigation of the influence of the solvent on the CL intensity, and (3) the addition of the well-known $^1O_2$ quencher NaN_3 to the aqueous peroxide reactions.

(1) Spectral Analysis of the VIS CL. All reactions depicted in Scheme 2 induce CL with an emission band in the 610−650 nm range and a second emission band which we monitored through a 700 nm interference filter. This is illustrated in Figure 1, which shows the CL spectrum of the MoO_4^{2-} induced decomposition of H_2O_2. These bands coincide with the position of the main radiative transitions of $(^1O_2)_2$ in the liquid phase:[9,27]

$$(^1\Delta_g)_{\nu=0}(^1\Delta_g)_{\nu=0} \rightarrow (^3\Sigma_g^-)_{\nu=0}(^3\Sigma_g^-)_{\nu=0} + h\nu\ (634\text{ nm})$$

$$(^1\Delta_g)_{\nu=0}(^1\Delta_g)_{\nu=0} \rightarrow (^3\Sigma_g^-)_{\nu=1}(^3\Sigma_g^-)_{\nu=0} + h\nu\ (703\text{ nm})$$

An additional emission band between 560 and 600 nm has been recorded in the acetone-induced decomposition of $KHSO_5$ in H_2O, Scheme 2a (Figure 1, Supporting Information (SI)), in the reactions of dimethyldioxirane with *N*-benzyl-4-piperidone (Figure 2, SI), and with 4-dimethylaminopyridine (Figure 3, SI) in CCl_4, Scheme 2d, as well as in the reactions of hydrogen peroxide with NCS and NBS, Scheme 2c (Figures 4 and 5, SI). This band may be assigned to the dimol transition:

$$(^1\Delta_g)_{\nu=1}(^1\Delta_g)_{\nu=0} \rightarrow (^3\Sigma_g^-)_{\nu=0}(^3\Sigma_g^-)_{\nu=0} + \mathrm{h}\nu\ (580\text{ nm})$$

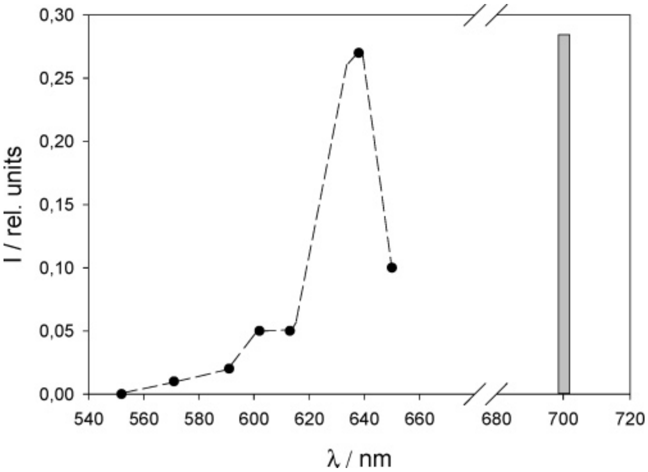


Figure 1. CL spectrum for the MoO_4^{2-} induced decomposition of hydrogen peroxide ($[Na_2MoO_4] = 2 \times 10^{-2}$ M, $[H_2O_2] = 2.2$ M, [KOH] = 0.1 M, H_2O, 20 °C). The bar indicates the CL signal recorded with the same reagent concentrations at 80 °C in 1:1 D_2O/H_2O with a 700 nm interference filter and a different photomultiplier.

A further CL band between 500 and 560 nm has been observed in the tertiary amine-induced decompositions of dimethyldioxirane (Figures 2 and 3, SI) and of H_2O_2 with NCS (Figure 4, SI). This emission is presumably caused by side reaction channels not associated with $(^1O_2)_2$.

Chemiluminescence during decomposition of DMNPO has already been reported earlier.[64,65] $(^1O_2)_2$ has been proposed to be responsible for the broad emission band near 675 nm in CCl_4[64] and for the weak luminescence near 700 nm in C_6D_6.[65] We found for the same CL system emission bands at 625 and 700 nm corresponding to $(^1O_2)_2$ emission (Figure 6, SI) in accordance with the previous results. Furthermore, we discovered that dimol CL may be observed not only in solution but also during decomposition of DMNPO on the surface of silica gel (Figure 7, SI) and aluminum oxide (Figure 8, SI). In contrast to the liquid-phase spectra, CL resulting from the surface reaction has further distinct emission bands below 600 nm. While the maximum at 580 nm may be explained by the $(^1\Delta_g)_{\nu=1}(^1\Delta_g)_{\nu=0} \rightarrow (^3\Sigma_g^-)_{\nu=0}(^3\Sigma_g^-)_{\nu=0}$ transition of $(^1O_2)_2$, the emission <560 nm is presumably caused either by impurities of the endoperoxide or by a new chemiluminescent channel in the endoperoxide decomposition on the surface, which is absent in solution. Actually, both Al_2O_3 and silica gel efficiently catalyze the decay of the endoperoxide. The activation parameters of the decomposition of DMNPO on silica gel (measured by NIR CL [1000−1300 nm] between 50 and 90 °C) lie in the range $E_a = 12.6-14.5$ kcal/mol, $\log(A/s^{-1}) = 6.1-7.3$ depending on the silica gel employed. On aluminum oxide, we determined $E_a = 17.4$ kcal/mol, $\log(A/s^{-1}) = 9$ (acid Al_2O_3); $E_a = 16.3$ kcal/mol, $\log(A/s^{-1}) = 8.4$ (neutral); $E_a = 13.0$ kcal/mol, $\log(A/s^{-1}) = 6.3$ (basic). Much higher values of $E_a = 24.8$ kcal/mol and $\log(A/s^{-1}) = 13.7$ have been determined for the decomposition of DMNPO in 1,4-dioxane.[50]

The appearance of the CL bands above 560 nm is similar for all reactions shown in Scheme 2. Furthermore, the ratio INT_{700}/INT_{625} of the time-integrated CL signals measured at 700 and 625 nm varies only little for the reactions studied, see Table 1.

TABLE 1: Ratio INT_{700}/INT_{625} of the Spectrally Uncorrected Time-Integrated CL Signals at 700 and 625 nm in Different Peroxide Reactions

peroxide reaction	$KHSO_5$ with acetone[a]	dioxirane with amine[b]	H_2O_2 with Na_2MoO_4[c]	H_2O_2 with NBS[d]	decomposition of DMNPO
INT_{700}/INT_{625}	3.8	2.8	2	1.9	3.5[e]; 3[f]

[a] $[KHSO_5] = 6.2 \times 10^{-2}$ M, [acetone] = 0.18 M, pH = 10 (0.6 M carbonate buffer), 20 °C, D_2O. [b] [dimethyldioxirane] = 4×10^{-2} M, [*N*-benzyl-4-piperidone] = 1×10^{-2} M, 30 °C, 1:1 $CDCl_3$/acetone. [c] $[H_2O_2] = 2.2$ M, $[Na_2MoO_4] = 2 \times 10^{-2}$ M, [KOH] = 0.1 M, 80 °C, 3:1 D_2O/H_2O. [d] $[H_2O_2] = 2$ M, [NBS] = 2×10^{-2} M, 40 °C, pH = 4 (0.5 M acetate buffer), 1:4 D_2O/H_2O. [e] [DMNPO] = 2×10^{-2} M, CCl_4, 70 °C. [f] [DMNPO] = 2×10^{-2} M, $CHCl_3$, 50 °C.

The moderate variation of the INT_{700}/INT_{625} values between 2 and 4 is possibly caused by the unavoidable changes of experimental conditions. To get reproducible and reliable CL signals, each of the peroxide reactions of Scheme 2 had to be studied at different temperatures and concentrations. It is very likely that luminescence intensities of $(^1O_2)_2$ at 634 and 703 nm depend in solution on temperature. Furthermore, in some cases, rather high peroxide concentrations have been used so that the emission could partially originate from $(^1O_2)_2$ inside of oxygen gas bubbles in contrast to the cases with low reagent concentrations, where the emission presumably stems only from $(^1O_2)_2$ dissolved in the liquid. This fact should additionally affect the INT_{700}/INT_{625} values because the radiative properties of the dimol and the quenching of the $(^1O_2)_2$ luminescence should be different in solution compared to the gas phase.

Moreover, the $^3O_2$ concentration also affects the ratio of integrated intensities of the dimol emission bands for the 0,0 (636 nm) and the 0,1 (706 nm) transitions in CCl_4, as was found in photosensitization experiments.[30] INT_{706}/INT_{636} decreases by 37% at room temperature, if the $^3O_2$ concentration increases from 3×10^{-4} to 1.24×10^{-2} M. We tested the effect of oxygen concentration on the CL emitted during the decomposition of DMNPO (1×10^{-2} M) in CCl_4 at 60 °C and observed a INT_{700}/INT_{625} diminution from 4.2 in argon saturated to 3.8 in oxygenated solution, which is in line with the findings of Chou et al.[30]

(2) Influence of the Solvent on the VIS CL. The lifetime τ_Δ of $^1O_2$ is strongly solvent dependent.[25] Since $^1O_2$ is the direct precursor of $(^1O_2)_2$, the intensity of singlet-oxygen dimol CL should also depend on solvent. We expect the time-integrated intensity INT_D of dimol CL observed through a 700 nm interference filter to follow eq 1 for first-order reactions, see Supporting Information.

$$INT_D = c_D k_{r,D} K f^2 (k_R/2) \tau_\Delta^{\,2} [P]_0^{\,2} \qquad (1)$$

$[P]_0$, k_R, f, K, $k_{r,D}$, and c_D are the concentration of the $^1O_2$ precursor P at time $t = 0$ of the start of reaction, the reaction rate constant, the efficiency of chemical $^1O_2$ production, the equilibrium constant of $(^1O_2)_2$ formation according to Scheme 1, the radiative rate constant of $(^1O_2)_2$, and the apparatus constant. Thus, INT_D should vary quadratically with τ_Δ for constant $[P]_0$, k_R, f, K, and $k_{r,D}$. This proportionality should be valid under the above conditions also for reactions of other orders. Therefore, INT_D should be larger for solvents with long $^1O_2$ lifetime, as CCl_4, compared with solvents of smaller τ_Δ, as acetone or CH_3CN, and for perdeuterated solvents compared with their common analogues.[14,25] To verify these expectations, we carried out a study on the influence of the solvent on the CL at 625 or 700 nm for the peroxide reactions a−e of Scheme 2.

The decomposition of DMNPO (e) is a first-order reaction. The integrated CL accompanying this reaction (2×10^{-2} M, 50 °C) is strongly solvent dependent. Relative values of INT_{700} normalized to the value in acetone are listed in Table 2. They increase strongly by a maximum factor of 220 (CCl_4). A similar

TABLE 2: Solvent Dependence of $^1O_2$ Lifetimes and Integrated CL Intensities for the Decomposition of 2×10^{-2} M DMNPO at 50 °C

solvent	$\tau_\Delta{}^0$/ms	τ_Δ/ms	τ_Δ/rel units	INT_{700}/rel units
CCl_4	128[66]	3.1	62	220
acetone-d_6	0.99[68]	0.77	15	8.8
acetonitrile	0.077[68]	0.075	1.5	2.2
acetone	0.051[68]	0.050	1	1

variation has been noticed for INT_{625}. If $[P]_0$, k_R, f, K, and $k_{r,D}$ do not change with solvent, eq 1 predicts a proportionality of INT_{700} with $\tau_\Delta{}^2$. Even if these quantities vary, the variation of τ_Δ should be dominant because of its tremendous graduations with solvent. In the absence of any quencher Q, when deactivation of $^1O_2$ occurs only by the solvent, $\tau_\Delta{}^0 = 1/k_\Delta$ holds true. Values of $\tau_\Delta{}^0$ increase from 50 μs in acetone to 128 ms in CCl_4, see Table 2. However, these lifetime are only valid for the pure solvents. Contaminations by impurities, reactants, intermediates, reaction products, and even $^3O_2$ lead to a reduction of τ_Δ, particularly in solvents of long lifetime. The presence of Q, which quenches $^1O_2$ with rate constant $k_\Delta{}^Q$, reduces the singlet-oxygen lifetime according to eq 2.

$$\tau_\Delta = (k_\Delta + k_\Delta{}^Q\,[Q])^{-1} \tag{2}$$

To estimate more realistic values of τ_Δ, we consider the $^1O_2$ quenching by $^3O_2$, with $k_\Delta{}^Q = 3.9 \times 10^4\ M^{-1}\ s^{-1}$ in CCl_4[66] and $[^3O_2] = 7.5 \times 10^{-3}$ M in oxygenated CCl_4 at 50 °C, and approximate the rate constant of $^1O_2$ quenching by DMNPO by $k_\Delta{}^Q = 1.4 \times 10^4\ M^{-1}\ s^{-1}$ determined for DMN in CCl_4.[67] Ignoring any further present source of $^1O_2$ quenching, we obtain for 2×10^{-2} M endoperoxide solutions the upper lifetime limits τ_Δ of Table 2. The graduation of the τ_Δ data is weaker than the graduation of INT_{700} indicating a stronger than linear dependence of INT_{700} on τ_Δ although the square dependence is not met. The consideration of the additional quenching by intermediates and reaction products, which is important in weakly deactivating solvents but cannot be performed, would certainly lead to a better approach to a square dependence of INT_{700} on τ_Δ. Thus, we conclude that these experiments give clear evidence for $(^1O_2)_2$ being present in this CL system.

The values of INT_{625} and INT_{700} have been found 24 and 33 times larger in D_2O than in H_2O for the acetone-catalyzed decomposition of potassium peroxymonosulfate, reaction a in Scheme 2, ($[KHSO_5] = 5.6 \times 10^{-2}$ M, [acetone] = 0.54 M, carbonate buffer (0.4 M) pH 10, 25 °C). Taking the corresponding $^1O_2$ lifetimes of 68 μs and 3.1 μs of the pure solvents into account and ignoring completely the additional quenching by reactants, intermediates, and reaction products, one estimates $\tau_\Delta = 64.4$ μs for 0.4 M H_2O in D_2O leading to $\tau_\Delta/\tau_{\Delta,H2O} = 21$.[25] Thus, again a stronger than linear dependence of the integrated CL signals on τ_Δ results, confirming the production of $(^1O_2)_2$ in that CL system. The INT_{575} value increased 12-fold under the same conditions indicating that this emission most probably corresponds to the $(^1\Delta_g)_{\nu=1}(^1\Delta_g)_{\nu=0} \rightarrow (^3\Sigma_g{}^-)_{\nu=0}(^3\Sigma_g{}^-)_{\nu=0}$ radiative transition.[9,27]

A 2.7- and 2-fold increase of INT_{700} was observed for the reactions of 2.2 M hydrogen peroxide with 2×10^{-2} M molybdate ions (b) ([KOH] = 0.1 M, 80 °C, H_2O vs 1.2:1 H_2O/D_2O) and with 2×10^{-2} M NBS (c) (acetate buffer, pH 4, 20 °C, H_2O vs 1:3 H_2O/D_2O). Considering only the different D_2O contents of the solvent mixtures, we calculate $\tau_\Delta/\tau_{\Delta,H2O}$ to be 1.8 and 3.5, respectively.

Finally, reaction d of 4.2×10^{-2} M dimethyldioxirane with the tertiary amine 4-dimethylaminopyridine in 1×10^{-2} M concentration was carried out at 20 °C in 1:1 acetone/acetone-d_6 and in 1:1 acetone/$CDCl_3$. The corresponding INT_{700} values were 1.8 and 10 times higher compared with pure acetone. Using the lifetimes given in Table 2, $\tau_\Delta = 5.6$ ms of oxygenated $CDCl_3$,[66,68] and ignoring any further quenching, the corresponding lifetime ratios $\tau_\Delta/\tau_{\Delta,acet}$ are estimated to be 1.9 and 2.0.

These experiments with different CL systems reveal that the variation of the solvent can tremendously influence the integrated dimol CL. A strong correlation of INT_D with the singlet-oxygen lifetime is found which reaches for the system with the lowest reagent concentration, the endoperoxide, the almost quadratic dependence expected from eq 1. A quantitative agreement is failed, most probably because of the systematically too large estimates for the singlet-oxygen lifetimes in the reaction solutions. Large deviations are expected for CL systems with high peroxide concentrations and fast reactions and in weakly deactivating solvents. The distinct deviation from quadratic dependence observed with the molybdate and dioxirane systems, however, could above that be caused by dimol emission from gas bubbles, evolving in these fast reactions. Because the reactants remain in the liquid phase, the dimol emission from gas bubbles will be much less reduced leading to smaller solvent effects.

(3) Quenching of the VIS CL by Sodium Azide. If experiments are performed in the same solvent and at the same temperature without and with quencher Q and with the same initial concentration of the reactant, then $[P]_0$, k_R, f, K, and $k_{r,D}$ should be constant and the corresponding ratio of the initial CL intensity maxima (see SI) should be given by eq 3.

$$I_{D,max}{}^0/I_{D,max} = (\tau_\Delta{}^0)^2\,(k_\Delta + k_\Delta{}^Q\,[Q])^2 \tag{3}$$

Then, we obtain the "Stern−Volmer" like relation 4,

$$(I_{D,max}{}^0/I_{D,max})^{0.5} - 1 = \tau_\Delta{}^0\,k_\Delta{}^Q\,[Q] \tag{4}$$

which demands that the square root of the initial dimol CL maxima ratio $I_{D,max}{}^0/I_{D,max}$ is linear with [Q] but not the ratio $I_{D,max}{}^0/I_{D,max}$ itself. Interestingly, the dimol emission quenching constant $K_D{}^Q = \tau_\Delta{}^0\ k_\Delta{}^Q$ is given as the product of the rate constant of monomol quenching and monomol lifetime. Sodium azide, an efficient water-soluble quencher of $^1O_2$, was employed to test its influence on the CL observed in peroxide reactions.[14] We found that NaN_3 quenches the initial CL intensity maximum of $(^1O_2)_2$ at 575, 625, and 700 nm arising in the reactions of H_2O_2 with Na_2MoO_4 and with NBS. This is illustrated for the molybdate system in Figure 2 displaying the dependences of $I_{700,\ max}$ and $(I_{700,max}{}^0/I_{700,max})^{0.5} - 1$ on $[NaN_3]$. In fact, a linear correlation of $(I_{700,max}{}^0/I_{700,max})^{0.5} - 1$ with $[NaN_3]$ was found. The slope is the dimol quenching constant $K_D{}^Q = 315\ M^{-1}$. Considering the deactivation contributions of H_2O and D_2O only, we estimate $\tau_\Delta{}^0 = 10.9$ μs. A time-resolved $^1O_2$ emission experiment (sensitizer: Rose Bengal) yields for the nonreactive 3:1 D_2O/H_2O mixture with 2.2 M H_2O_2 and 0.1 M KOH, but without molybdate, at 20 °C expectedly the smaller value $\tau_\Delta{}^0 = 7.0$ μs. Neglecting the unknown quenching by reactants and intermediates at 80 °C, we calculate with this $\tau_\Delta{}^0$ value $k_\Delta{}^Q = 4.5 \times 10^7\ M^{-1}\ s^{-1}$ as rate constant of $^1O_2$ quenching by sodium azide.

Although a strong dimol emission quenching and the requested linear correlation of eq 4 have been found, the value of $k_\Delta{}^Q$ resulting from the dimol quenching is significantly smaller than $k_\Delta{}^Q = 5.0 \times 10^8\ M^{-1}\ s^{-1}$ measured by us for the monomol quenching by NaN_3 in 3:1 D_2O/H_2O with 2.2 M H_2O_2 and 0.1 M KOH at 20 °C in photosensitized experiments, where the

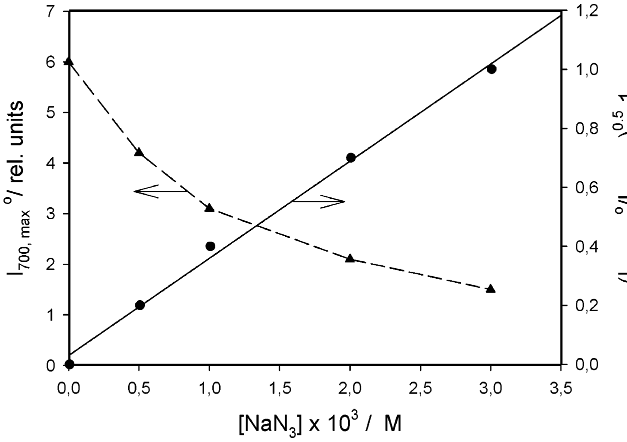


Figure 2. Dependence of $I_{700,max}{}^0$ and $(I_{700,max}{}^0/I_{700,\ max})^{0.5} - 1$ on [NaN_3] for the molybdate-catalyzed decomposition of H_2O_2 (3:1 D_2O/H_2O, [Na_2MoO_4] = 2 × 10^{-2} M, [H_2O_2] = 2.2 M, [KOH] = 0.1 M, 80 °C).

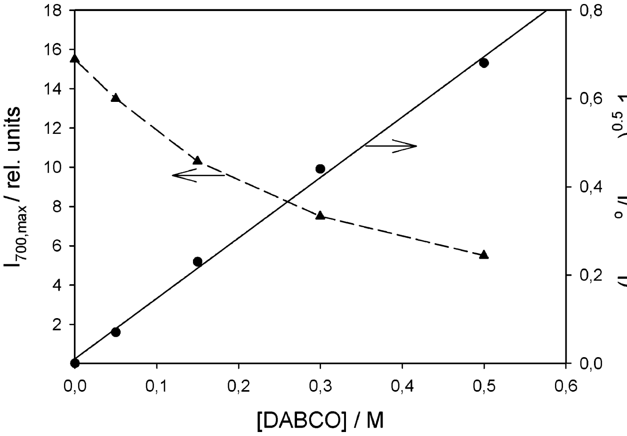


Figure 3. Dependence of $I_{700,max}$ and $(I_{700,max}{}^0/I_{700,max})^{0.5} - 1$ on DABCO concentration for the molybdate-catalyzed decomposition of H_2O_2 ([Na_2MoO_4] = 2 × 10^{-2} M, [H_2O_2] = 2.2 M, [KOH] = 0.1 M, 4.7:1 D_2O/H_2O, 80 °C).

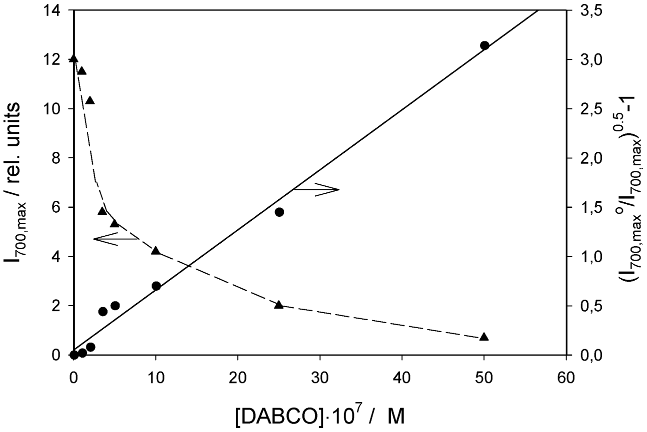


Figure 4. Dependence of $I_{700,max}$ and $(I_{700,max}{}^0/I_{700,max})^{0.5} - 1$ on DABCO concentration for the decomposition of 1,4-dimethylnaphthalene endoperoxide ([DMNPO] = 5 × 10^{-4} M, CCl_4, 60 °C).

additional quenching of reaction intermediates and products is missing. It could well be that the graduation of $k_\Delta{}^Q$ reflects a corresponding variation of the $^1O_2$ lifetime between the reacting CL system and the nonreactive solution. If this holds true, the actual $^1O_2$ lifetime would have been about 0.6 μs in the CL system.

In summary, the spectral analysis of CL and the effects of solvent and NaN_3 on CL intensity consistently demonstrate that singlet oxygen dimol is at least the principal emitter of the CL observed at $\lambda > 570$ nm in the reactions a−e of Scheme 2.

Effect of DABCO on Singlet-Oxygen Dimol CL. Using the above characterized convenient chemical sources of $(^1O_2)_2$, we investigated the controversial influence of DABCO on the dimol CL. Our results show that DABCO enhances dimol CL in none of the reactions a−e of Scheme 2. In contrast, strong quenching of the $(^1O_2)_2$ emission has been observed. This was the result of qualitative experiments performed on the acetone-induced decomposition of $KHSO_5$ (a) ([$KHSO_5$] = 5.6 × 10^{-2} M, [acetone] = 0.54 M, 0.6 M carbonate buffer pH = 10, D_2O, 20 °C) and on the reaction of dimethyldioxirane with tertiary amines[69] (d) ([dioxirane] = 4 × 10^{-2} M, [4-dimethylaminopyridin] = 8 × 10^{-3} M, acetone, 20 °C). The results of quantitative experiments are illustrated in Figures 3 and 4 for the molybdate-induced decay of hydrogen peroxide (b) and the decomposition of DMNPO (e), respectively. A linear variation of $(I_{700,max}{}^0/I_{700,max})^{0.5} - 1$ with [DABCO] has also been found for the reaction of NBS with H_2O_2 (c). Evaluation according to eq 4 yields the quenching constants $K_D{}^Q$ listed in Table 3.

For the molybdate/H_2O_2 and NBS/H_2O_2 systems, small quenching constants are obtained which lead with the corresponding experimental $^1O_2$ lifetimes $\tau_\Delta{}^0$ to rate constants $k_\Delta{}^Q$ of 1.8 × 10^5 (molybdate) and 3.8 × 10^5 M^{-1} s^{-1} (NBS).[70] The value found for the molybdate system is about 5 times smaller than $k_\Delta{}^Q = 1.0 \times 10^6$ M^{-1} s^{-1} determined for the quenching of $^1O_2$ by DABCO in our photosensitized emission experiments in the corresponding nonreactive solvent mixture, which is in agreement with literature values on quenching of singlet oxygen by DABCO in water.[71] We assume that similarly to the case of dimol CL quenching by NaN_3, vide infra, the actual lifetime of $^1O_2$ is much shorter in that CL system than in the nonreactive solvent mixture.

The assumption that high reagent concentrations reduce the $^1O_2$ lifetime and concomitantly diminish the quenching constants of dimol CL emission is confirmed by the experiments with DMNPO. A very large dimol CL emission quenching constant of $K_D{}^Q = 6.0 \times 10^5$ M^{-1} resulted for DABCO in diluted solutions of DMNPO (5 × 10^{-4} M) in CCl_4. Considering only $^1O_2$ quenching by $^3O_2$ and DMNPO, we estimate as described above $\tau_\Delta{}^0 = 22.4$ ms for oxygenated CCl_4 at 60 °C. That guess leads to $k_\Delta{}^Q = 2.7 \times 10^7$ M^{-1} s^{-1} as rate constant of $^1O_2$ quenching by DABCO, which agrees with $k_\Delta{}^Q = 4.4 \times 10^7$ M^{-1} s^{-1} determined for $^1O_2$ quenching by DABCO in photosensitization experiments in CCl_4 (with 1 vol % of C_6H_6 for suppression of the otherwise multiexponential decay of $^1O_2$ emission) confirming the validity of eq 4. Thus, the results obtained with NaN_3 and DABCO convincingly prove that in the CL systems investigated quenching of $(^1O_2)_2$ dimol luminescence is linked together with the quenching of $^1O_2$ via their very fast formation and dissociation equlibrium.

It is very interesting that DABCO quenches the $(^1O_2)_2$ CL not only in solution but also on the surface of Al_2O_3. The integrated CL signal observed at $\lambda > 600$ nm during the reaction of 1 × 10^{-4} M/g DMNPO supported on acid Al_2O_3 is in the presence of DABCO (2 × 10^{-4} M/g supported on acid Al_2O_3) at 60 °C 5 times lower than in the absence of the cyclic amine. This result further demonstrates that singlet-oxygen dimol CL emission is quenched by the addition of DABCO.

However, puzzling observations still exist. We briefly checked the ClO^-/H_2O_2 system and confirmed the reported increase of VIS CL (>600 nm) upon addition of DABCO.[33−35,45] It was suggested that one reason for such an intensification could be the change "in the rate or extent of nucleation of oxygen

TABLE 3: Constants $K_D^Q = \tau_\Delta^0 k_\Delta^Q$ of Dimol CL Quenching by DABCO, Estimated and Experimental $^1O_2$ Lifetimes τ_Δ^0, and Rate Constants k_Δ^Q of $^1O_2$ Quenching by DABCO in CL and Photosensitization Experiments[a]

CL reaction	K_D^Q/M^{-1}	τ_Δ^0/s[f]	τ_Δ^0/s[g]	k_Δ^Q/M^{-1} s^{-1} [h]	k_Δ^Q/M^{-1} s^{-1} [i]
(b) molybdate/H_2O_2[b]	1.4	14×10^{-6}	7.8×10^{-6}	1.8×10^5	1.0×10^6
(c) NBS/H_2O_2[c]	2.3	5.3×10^{-6}	6.0×10^{-6}	3.8×10^5	5.4×10^5
(e) endoperoxide[e]	6.0×10^5	22.6×10^{-3}		2.7×10^7	4.4×10^7

[a] Rose Bengal and 1-H-phenalen-1-one were used as sensitizers for the reactions b, c, and e. [b] [Na_2MoO_4] = 0.02 M, [H_2O_2] = 2.2 M, [KOH] = 0.1 M, 4.7:1 D_2O/H_2O, 80 °C. [c] [NBS] = 0.02 M, [H_2O_2] = 2 M, 0.2 M acetate buffer pH = 4.8, 1.3:1 H_2O/D_2O, 40 °C. [e] 5×10^{-4} M DMNPO in CCl_4 at 60 °C. [f] Considering only quenching by the solvent components, endoperoxide, and O_2. [g] Experimental $^1O_2$ lifetime τ_Δ^0 in the respective solvent mixtures without molybdate, NBS, or DMNPO. [h] Calculated if possible from experimental τ_Δ^0 data and K_D^Q. [i] Rate constant of $^1O_2$ quenching by DABCO determined in the corresponding solvent mixtures at 20 °C by photosensitization.

bubbles".[34] However, we found that even for 1×10^{-3} M hypochlorite and 1×10^{-3} M hydrogen peroxide VIS CL emission is still enhanced by DABCO. It is unlikely that VIS CL comes from $(^1O_2)_2$ inside oxygen bubbles at these low reactant concentrations but rather from dissolved excited species.

Thus, it seems that other still unknown intermediates than $(^1O_2)_2$, which emit in the same spectral region and which are produced by direct oxidation of DABCO or by interaction with reactive peroxide impurities presented in the aqueous ClO^-/H_2O_2 and disodium 3,3′-(1,4-naphthylidene)dipropionate endoperoxide systems,[33−35,45] are responsible for the observed increase of the VIS CL. The speculation that this increase of CL could be caused by a tremendous enhancement of the radiative probability of the dimol similarly to the binary complexes of $(^1O_2)_2$ and some dyes[43] seems not to hold true for DABCO. In that case, dimol CL enhancement should also have been found for the CL systems of Scheme 2 of the present study. A complementary study on the influence of DABCO on the emission of photophysically produced $(^1O_2)_2$ will address this problem in more detail.[72]

Conclusions

We have shown by spectral analysis and investigation of solvent as well as by quencher effects that the CL in the visible spectral region of five different peroxide reactions (Scheme 2) originates from $(^1O_2)_2$ singlet-oxygen dimol species. The results can quantitatively be described on the basis of a very fast formation and dissociation equilibrium between $(^1O_2)_2$ and $^1O_2$. Our results demonstrate that in none of the reactions shown in Scheme 2 does DABCO enhance CL of $(^1O_2)_2$. In contrast, strong quenching of the CL is observed so that DABCO cannot be a reliable chemiluminescent probe for the involvement of $^1O_2$ and $(^1O_2)_2$ species in chemical and biological systems. The question on the reason of the enhancement of the VIS CL generated by the hypochlorite/hydrogen peroxide reactions and by the thermolysis of disodium 3,3′-(1,4-naphthylidene)dipropionate endoperoxide is still open and requires further study.[33−35,45]

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Supporting Information Available: Chemiluminescence spectra (taken by means of cutoff filters) recorded in the peroxide reactions and the derivation of kinetic equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(69) Although a quenching of dimol CL by DABCO has been observed, it was not possible to perform an adequate quantitative interpretation of the results since dimethyldioxirane was found to be efficiently reactive with DABCO.

(70) Notably, photosensitized $^1O_2$ emission quenching experiments with DABCO showed an unusual behaviour in the acidic solvent mixture. Addition of the quencher did not affect the singlet-oxygen lifetime in the low [DABCO] range. Presumably, DABCO becomes protonated and thus is a much less effective quencher as long as the buffer keeps the pH in the acidic range. Only above [DABCO] = 0.127 M a linear increase of $\tau_\Delta{}^0/\tau_\Delta$ with [DABCO] was observed yielding $k_\Delta{}^Q = 5.4 \times 10^5$ M^{-1} s^{-1} as rate constant of $^1O_2$ quenching by DABCO, which compares well with $k_\Delta{}^Q = 3.8 \times 10^5$ M^{-1} s^{-1} obtained for dimol quenching by DABCO in the NBS/H_2O_2 system (Table 3). Agreement of values of $k_\Delta{}^Q$ determined in CL and in photosensitization experiments would quantitatively prove eq 4. However, because of the observed pH effect, it is open whether the agreement of the rate constants is possibly accidental.

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