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A pulse radiolysis and pulsed laser study of the pyrromethene 567 triplet state

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Abstract

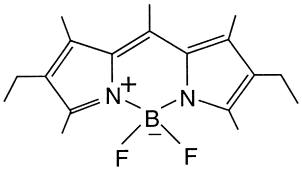
The triplet state of pyrromethene 567, a molecule with potential as a solid state laser dye, has been characterized in benzene by pulse radiolysis in terms of its absorption spectrum, lifetime, self-quenching, electronic excitation energy, triplet–triplet extinction coefficient and oxygen quenching rate constant. The use of laser flash photolysis has then allowed determination of the triplet quantum yield, efficiency of formation of singlet oxygen ($^1\Delta_g$), and the rate constant for reaction of the latter species with the ground state. The affects of oxygen on the fluorescence and triplet yields demonstrate that oxygen-induced intersystem crossing is important, the sum of these parameters being unity within experimental error. The mechanism of reaction of P-567 with $^1\Delta_g$ in benzene is predominantly physical in character with only a small (~6%) contribution from chemical reaction. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Pyrromethane 567; Dye fading; Triplet states; Singlet oxygen; Chemical quenching

1. Introduction

The development of tunable solid state dye lasers in which a polymer or glass host medium is doped with the appropriate dye is an area of active research and development. Such lasers potentially offer the performance of a normal tunable solution dye laser combined with the convenience of the solid state counterpart. The nature of the active element makes them inexpensive and potentially commercially important tunable laser sources. Although dye-doped elements, excited in a laser cavity by the second harmonic of a Q-switched Nd : YAG laser, have exhibited tunability greater than 50 nm [1], greater than 70% slope efficiency [2,3], operation for more than 10^5–$10^6 \sim 10$ mJ pulses [4] and bandwidths of less than 500 MHz [5], these performances have not been achieved at the same time. A particular problem is the gradual loss of performance, presumed to be due to the photodegradability of the guest dye, clearly a critical characteristic in this scenario.

In the late 1980's Pavlopoulos, Boyer and co-workers developed the pyrromethene family of dyes which promised enhanced laser efficiency and photstability [6–10]. In particular, the dye **1**, a pyrromethene-BF$_2$ complex known as pyrromethene 567 (P-567), which shows excellent solution performance in both time-resolved and steady-state modes [11–13], has been reported to exhibit a 77% slope efficiency in polymethylmethacrylate [2] and only a 25% efficiency loss after 8×10^4 pulses pumped with a fluence of 0.16 J cm^{-2} [14]. It has been shown in one of our laboratories [15] and elsewhere [16,17] that although the lasing efficiency of P-567 in polymethylmethacrylate, sol-gel glass and a composite thereof is excellent, the issue of photostability is absolutely crucial. Preliminary evidence has indicated that the presence of oxygen is important to the photodegradation mechanism [18] and improved performance of P-567 in deoxygenated solid-state hosts has been demonstrated [19].



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The aim of the current work was to characterise the triplet state of P-567 and decide whether or not a significant amount of this species is produced on direct excitation of the dye. If so, the questions to be addressed were (a) to what extent does this lead to the formation of singlet oxygen , $^1\Delta_g$, in aerated medium and (b) is this species responsible for dye degradation? The results are described in the following sections.

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2. Experimental

2.1. Materials

2-acetonaphthone [20], acridine [20], anthracene [21], benzene [20], benzophenone [22], biphenyl [22], naphthalene [20] and perylene [21] were as previously described. Benzene-d_6 (Aldrich, 99.6 at.%), chloroform-d_1 (Aldrich, 99.8 at.%), P-567 (Exciton Laser Dyes Inc.) and tetraphenylporphyrin (Aldrich) were used as received.

2.2. Time-resolved techniques

Pulse radiolysis [23] and pulsed laser [24] techniques were as described. Singlet oxygen 1267 nm emission detection was essentially as described [22]. All time-resolved experiments were single shot on fresh solutions.

3. Results and discussion

The triplet state of P-567 has been fully characterised using a combination of pulse radiolysis and direct laser excitation. The relevant parameters are summarised in Table 1.

3.1. Production of $^3P\text{-}567^*$ by pulse radiolysis in benzene

Eqs. (1)–(6) summarise the events which occur as a consequence of pulse radiolysis of a solution of benzene (B) containing 2-acetonaphthone (2-A; 1×10^{-2} mol l^{-1}) and P-567 (1×10^{-4} mol l^{-1}). The intense absorption of P-567 centered at 521 nm (Fig. 1) meant that optical analysis over the whole spectral range required low concentrations of this species. Since the lifetime of $^3B^*$ in benzene is only a few nanoseconds, a long-lived carrier triplet was required as an intermediary (cf. [20]), hence the use of 2-A. In Fig. 2 are shown the transient spectral changes for such an experiment as a function of time. These clearly show the ground-state bleaching of P-567 at 521 nm and the triplet absorption maxima at 450 and 700 nm. The first-order constant for growth of ^{3}P-567* via channel 6 (cf. Fig. 2 (inset 1)) corresponded to a rate constant for triplet energy transfer of 6.2×10^9 l mol^{-1} s^{-1}, typical of an exothermic process in

$$\mathrm{B} \xrightarrow{e} {}^1\mathrm{B}^* \text{ and } {}^3\mathrm{B}^* \tag{1}$$

$${}^1\mathrm{B}^* \rightarrow {}^3\mathrm{B}^* \tag{2}$$

$${}^1\mathrm{B}^* + \text{2-A} \rightarrow \mathrm{B} + {}^1\text{2-A}^* \tag{3}$$

$${}^3\mathrm{B}^* + \text{2-A} \rightarrow \mathrm{B} + {}^3\text{2-A}^* \tag{4}$$

$${}^1\text{2-A}^* \rightarrow {}^3\text{2-A}^* \tag{5}$$

$${}^3\text{2-A}^* + \text{P-567} \rightarrow \text{2-A} + {}^3\text{P-567}^* \tag{6}$$

benzene. The decay of ^{3}P-567* shown in Fig. 2 (inset 2) was not exponential but typical of competition between T–T annihilation and natural triplet decay, the competing first and second order fit giving a triplet lifetime, k_d^{-1} of 282 μs and a T–T annihilation rate constant, $2k_{TT} = 2.5\times10^9$ l mol^{-1} s^{-1}, utilising the triplet extinction coefficient determined as per Section 3.4. The first-order component was independent of P-567 ground-state concentration up to 1×10^{-3} mol l^{-1} indicating the absence of significant self quenching, $k_{sq} \leq 10^6$ l mol^{-1} s^{-1}. In aerated benzene ^{3}P-567* decay was strictly exponential, the first-order rate constant corresponding to an oxygen quenching rate constant, k_{ox}, of 1.5×10^9 l mol^{-1} s^{-1}, typical of triplet states in general.

3.2. Formation of ^{3}P-567* on direct excitation

Laser excitation of P-567 in deaerated benzene at either 355 or 532 nm yielded the same species characterised as ^{3}P-567* by pulse radiolysis, as shown by identical spectral

Table 1
Key photophysical parameters concerning P-567 in benzene

Triplet-ground state absorption	$\lambda_{max} = 450$ nm (13280)[a], 700 nm (6600)[b]
Triplet lifetime	$\tau_T = 282 \pm 28$ μs
Triplet energy	$E_T = 37.9 \pm 0.1$ kcal mol^{-1}
Triplet self-quenching	$k_{sq} \leq 1.0\times10^6$ l mol^{-1} s^{-1}
Triplet oxygen quenching	$k_{ox} = 1.5\times10^9$ l mol^{-1} s^{-1}
Fluorescence yield (aerated)	$\phi_F = 0.88 \pm 0.04$
Fluorscence yield (deaerated)	$\phi_F = 1.0 \pm 0.05$
Triplet yield (aerated)	$\phi_T = 0.09 \pm 0.009$
Triplet yield (deaerated)	$\phi_T = 0.03 \pm 0.005$
Singlet oxygen yield (aerated)	$\phi_\Delta = 0.09 \pm 0.009$
Oxygen quenchings giving $O_2(^1\Delta_g)$	$S_\Delta = 1.0 \pm 0.2$[c]
Singlet oxygen quenching	$k_\Delta = 3.0\times10^7$ l mol^{-1} s^{-1}[d]
T–T annihilation	$2k_{TT} = 2.5\times10^9$ l mol^{-1} s^{-1}

[a] S_0–T_1 difference coefficient.
[b] Absolute extinction coefficient.
[c] Based on the experimental errors for ϕ_T and ϕ_Δ.
[d] Determined in benzene-d_6.

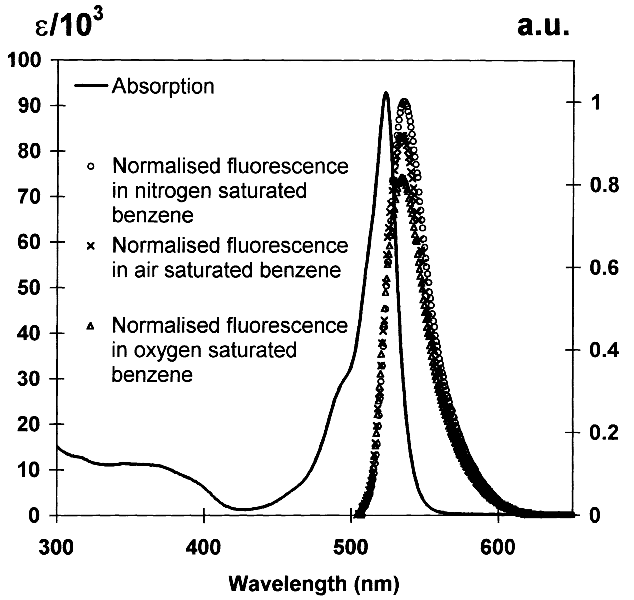

Fig. 1. Electronic absorption and normalized fluorescence spectra of P-567 in benzene.

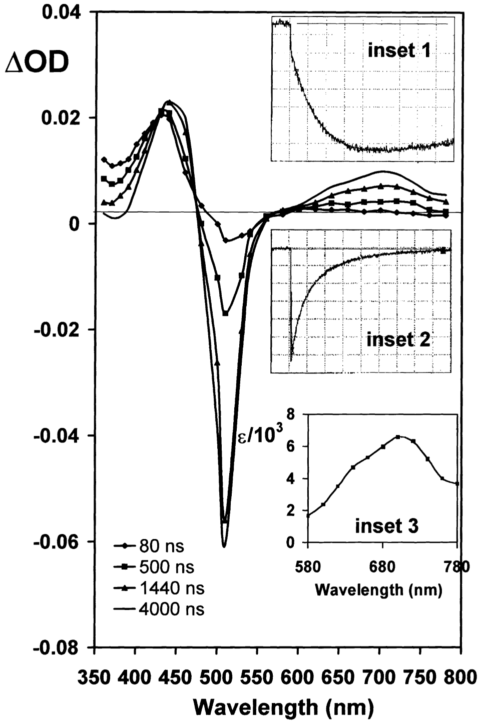

Fig. 2. Transient difference absorption spectra as a function of time after absorption of a 20 ns electron pulse by deaerated benzene containing 2-A (10^{-2} mol l^{-1}) and P-567 (10^{-4} mol l^{-1}) with delays after the pulse as shown. Insets: (1) corresponding time-dependence of transient absorption monitored at 700 nm with consecutive first-order fit, $k_1 = 6.2 \times 10^5$ s^{-1}, $k_2 = 2.8 \times 10^4$ s^{-1}, 1.6% absorption/division, 1 μs/division. (2) as for (1) at 700 nm with competing second- and first-order fit, $2k_{1/\varepsilon} = 3.8 \times 10^5$ cm s^{-1}, $k_2 = 3.6 \times 10^3$ s^{-1}, 1.1% absorption/division, 100 μs/division. (3) absolute absorption spectrum of the P-567 triplet state above 580 nm including the spectral region of laser operation.

characteristics. Again the decay contained a second-order component which disappeared at very low laser energies and low P-567 concentrations. The triplet energy of this species was determined as described below.

3.3. Determination of the triplet energy of P-567

We have routinely determined triplet energies by establishment of equilibria for triplet energy transfer between a molecule of interest and a sensitizer of known triplet energy (cf. [21] and references therein). By sequentially lowering the triplet energy of the triplet carrier by replacing 2-A ($E_T = 59.6$ kcal mol^{-1}) in pulse radiolysis experiments (cf. Eqs. (3)–(6)) with acridine ($E_T = 45.0$ kcal mol^{-1}), anthracene ($E_T = 42.7$ kcal mol^{-1}) and perylene (Pe; $E_T = 35.1$ kcal mol^{-1}) we have shown that triplet energy transfer to P-567 remains exothermic until, in the case of Pe, no ^{3}P-567* grow-in is observed under the same concentration conditions. The indication that the triplet energy of P-567 lies between those of anthracene and Pe has been confirmed. Thus, pulse radiolysis of a deaerated benzene solution of P-567 (4.7×10^{-3} mol l^{-1}) and Pe (4.7×10^{-5} mol l^{-1}), i.e. only ca. 1% of the energy going into Pe, resulted in 'immediate' formation of ^{3}P-567*, monitored at 700 nm where ^{3}Pe* does not absorb. The decay at 700 nm was biexponential, showing fast decay to equilibrium followed by slow bleeding of that equilibrium (cf. Eq. (7) and Fig. 3). Extrapolation of the fast and slow

$$^3\text{P-567}^* + \text{Pe} \quad \rightleftarrows \quad \text{P-567} + {^3\text{Pe}^*} \qquad (7)$$

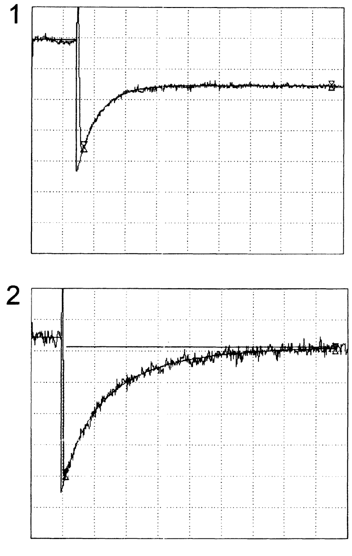

Fig. 3. Transient absorption at 700 nm as a function of time after absorption of a 20 ns electron pulse by deaerated benzene containing Pe (5.0×10^{-5} mol l^{-1}) and P-567 (4.7×10^{-3} mol l^{-1}), (1) with consecutive first-order fit, $k_1 = 6.4 \times 10^5$ s^{-1}, $A_0 = 2.0 \times 10^{-2}$; $k_2 = 2.0 \times 10^4$ s^{-1}, $A_e = 8.2 \times 10^{-3}$, 1.3% absorption/division, 2 μs/division and (2) with first-order fit, $k' = 6.7 \times 10^3$ s^{-1}, 0.41% absorption/division, 50 μs division.

decays to time zero gave optical densities corresponding to the concentrations of ^{3}P-567* initially, A_0, and at equilibrium, A_e. Because decay to equilibrium is very fast relative to subsequent decay (cf. Fig. 3(1)), the equilibrium constant is given by $K = [\text{P-567}]\,[A_0 - A_e]\,[\text{Pe}]^{-1}[A_e]^{-1} = 85 \pm 17$ corresponding to $\Delta G = -2.6 \pm 0.1\,\text{kcal mol}^{-1}$. The standard assumption of no entropy change gives an E_T value of $37.7 \pm 0.1\,\text{kcal mol}^{-1}$ for P-567. Such determinations are accurate due to the exponential relationship between K and ΔG, a large error in K resulting in a small error in ΔG.

3.4. *Triplet–triplet extinction coefficient of ^{3}P-567**

We have used the well-documented technique of Bensasson and Land [25] to determine the T–T extinction coefficient of ^{3}P-567*. In these experiments biphenyl (BP) replaced 2-A (cf. Eqs. (1)–(6)) as the triplet energy carrier due to its more intense and shorter wavelength T–T absorption at 370 nm. Thus, deaerated benzene solutions of BP ($10^{-1}\,\text{mol l}^{-1}$), both with and without the presence of P-567 ($10^{-4}\,\text{mol l}^{-1}$) were subjected to pulse radiolysis at identical radiation doses. Under these conditions the initial yield of ^{3}BP*, produced as a consequence of processes corresponding to channels 1–5, will be identical with and without P-567. Since we have also shown that triplet energy transfer from ^{3}BP* to P-567 occurs with a rate constant of $1.0 \times 10^{10}\,\text{l mol}^{-1}\,\text{s}^{-1}$ and the natural decay constant of ^{3}BP* is $2.0 \times 10^{-4}\,\text{s}^{-1}$, under these conditions, 98% of donor triplets were scavenged by P-567. The initial donor triplet optical density (OD) at 370 nm from the blank experiment and the OD of ^{3}P-567* extrapolated to time zero as per Fig. 1 (inset 2), coupled with the published T–T extinction coefficient of BP at 370 nm [25] then yielded the corresponding values for P-567 at 450 nm (13,280 $\text{l mol}^{-1}\,\text{cm}^{-1}$; $S_0 - T_1$ difference coefficient) and 700 nm (6600 $\text{l mol}^{-1}\,\text{cm}^{-1}$; absolute T_1 coefficient).

3.5. *Determination of the triplet quantum yield*

Determination of the P-567 triplet yield required comparison with a standard of known ϕ_T and T–T extinction coefficient. The standard chosen involved excitation of benzophenone at 355 nm in benzene containing naphthalene (N; $10^{-1}\,\text{mol l}^{-1}$). Under these conditions the yield of ^{3}N* is unity [22]. Thus, optically matched solutions ($\text{OD}_{355} = 0.49$) of the standard and P-567 in aerated and deaerated benzene were subjected to laser flash photolysis. Plots of triplet OD's at λ_{max}, extrapolated to time 0, as a function of laser energy (cf. Fig. 4), together with the known extinction coefficients of ^{3}N* [25] and ^{3}P-567* (this work) yielded values of ϕ_T for P-567 of 0.09 and 0.03 in aerated and deaerated benzene, respectively.

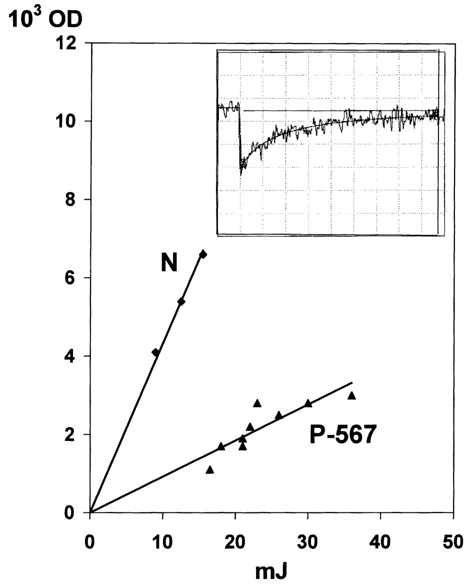

Fig. 4. Plot of optical density extrapolated to time zero, OD_0, as a function of laser energy for optically matched deaerated benzene solutions subjected to laser excitation at 355 nm ($\text{OD}_{355} = 0.49$) and containing benzophenone and N ($10^{-1}\,\text{mol l}^{-1}$), ^{3}N* monitored at 423 nm and P-567, ^{3}P-567* monitored at 450 nm. Inset: transient absorption for a P-567 experiment with competing second- and first-order fit, $26 \times 0.162 = 4.2$ mJ, 0.2% absorption/division, 200 μs/division, $\text{OD}_0 = 2.2 \times 10^{-3}$. The laser energies on the abscissa are before attenuation to 16.2% by means of neutral density filters.

3.6. *Determination of the singlet oxygen quantum yield*

We have measured the singlet oxygen quantum yield, ϕ_Δ, for P-567 by laser excitation of optically matched solutions (OD = 1.0) of P-567 and tetraphenylporphyrin (TPP) as standard ($\phi_\Delta = 0.62$ [26]) in aerated benzene using both 355 and 532 nm excitation. Plots of the 1267 nm luminescence extrapolated to time zero, I_Δ against laser energy (Fig. 5) allowed the yield for P-567 to be determined. Values for both wavelengths were within experimental error of each other, $\phi_\Delta = 0.09$. This value is identical to the triplet yield in aerated benzene.

3.7. *Determination of the fluorescence quantum yield*

The increase in the triplet yield in benzene on aeration (cf. Section 3.5) clearly indicated the importance of oxygen-induced intersystem crossing. This was supported by fluorescence spectra (cf. Fig. 1) and quantum yield measurements which were determined using fluorescein dianion in ethanol as the standard [27]. Values of ϕ_F, corrected for refractive index differences, were 1.0 ± 0.05 and 0.88 ± 0.04 in deaerated and aerated benzene, respectively.[1]

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[1] Previously reported values in methanol (presumably aerated) are 0.83 [5,6] and 0.995 [12].

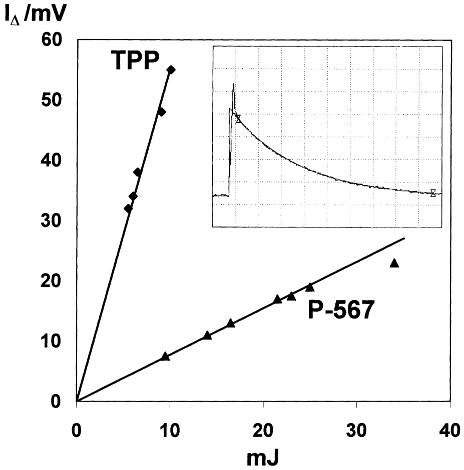

Fig. 5. Plots of emission intensity at 1267 nm, extrapolated to time zero, I_Δ as a function of laser energy for optically matched aerated benzene solutions of TPP and P-567 subjected to laser excitation at 532 nm ($OD_{532} = 1.0$). Inset: corresponding time dependence of emission for P-567 with first-order fit, $25 \times 0.03 = 0.84$ mJ, 5 mV/division, 10 μs/division, $I_\Delta = 19.2$ mV. The laser energies on the abscissa are before attenuation to 3% by means of neutral density filters.

3.8. *Quenching of singlet oxygen by P-567*

Preliminary experiments demonstrated that the quenching of $^1\Delta_g$ by P-567 is relatively inefficient at available concentrations. In order to facilitate the determination of an accurate rate constant the reaction was examined in benzene-d_6 for which the $^1\Delta_g$ lifetime is ∼620 μs compared with 33 μs in benzene [28]. Thus, laser excitation of 2-A at 355 nm in aerated benzene-d_6 containing varying P-567 concentrations allowed the first-order rate constant, k', for the decay of the 1267 nm luminescence of $^1\Delta_g$ to be monitored as a function of P-567 concentration. A standard Stern–Volmer plot gave a rate constant for quenching, k_Δ, of 3.0×10^7 l mol s^{-1}. This rate constant could reflect physical and/or chemical contributions to quenching. Only the latter contribution would be of consequence to dye degradation and we have attempted to determine its importance as outlined below.

3.9. *Chemical versus physical quenching of singlet oxygen*

If a significant fraction of the quenching of $^1\Delta_g$ by P-567 were chemical in character it would, in principle, be possible to make a direct comparison of $^1\Delta_g$ -induced bleaching of P-567 with that of 1,3-diphenylisobenzofuran (DBPF), an exclusively chemical quencher of $^1\Delta_g$ [22,29,30] using pulse radiolysis as already described [20]. Such a procedure turned out to be difficult to perform in practice, principally because of the intense ground state absorption of P-567 which meant that only relatively low concentrations of this quencher could be used despite the fact that its rate constant for quenching of $^1\Delta_g$ is some 30-fold smaller than that for DPBF, i.e. a less than ideal fraction of the $^1\Delta_g$ produced would be scavenged. This fraction was optimised by performing the experiments in benzene-d_6. Thus, aerated solutions of biphenyl (3×10^{-2} mol l^{-1}) containing either DPBF or P-567 (10^{-4} mol l^{-1}) were subjected to identical pulse radiolysis experiments and the bleaching of both $^1\Delta_g$ quenchers examined (Fig. 6). The bleaching signal for P-567 was clearly much weaker and much more slowly formed than for DPBF as anticipated. Calculation of the amounts of $^1\Delta_g$ scavenged in each case from quenching rate constants and τ_Δ, together with the known quencher extinction coefficient at each monitoring wavelength, indicated chemical bleaching of no more than ∼6% in the case of P-567.[2] This would correspond to a chemical quenching rate constant in the 10^6 s^{-1} range, certainly significant.

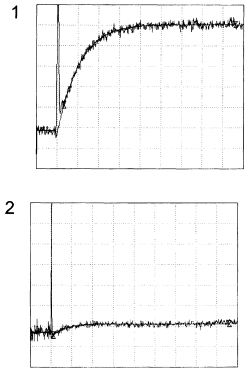

Fig. 6. Bleaching of ground states after pulse radiolysis (500 ns pulse) of an aerated benzene-d_6 solution of biphenyl (3×10^{-2} mol l^{-1}) containing (1) DPBF (1×10^{-4} mol l^{-1}), monitored at 415 nm ($\varepsilon = 2.2 \times 10^4$ l mol^{-1} cm^{-1}), 7.8% absorption/division, 10 μs/division, $k' = 1.0 \times 10^5$ s^{-1} and (2) P-567 (1×10^{-4} mol l^{-1}), monitored at 480 nm ($\varepsilon = 1.7 \times 10^4$ l mol^{-1} cm^{-1}), 0.45% absorption/division, 500 μs/division, $k' = 3.3 \times 10^3$ s^{-1}.

4. Conclusions

The triplet state of P-567 has been unambiguously generated and characterized by pulse radiolysis. It has been shown that the same species is indeed produced on direct excitation into either S_1 or S_2 with a yield of ∼3% in deaerated medium. The yield increases with aeration of the medium. The corresponding fluorescence quantum yields support the operation of an oxygen-induced intersystem crossing process since the sum of ϕ_F and ϕ_T remains unity within experimental error. The fact that ϕ_Δ is the same as ϕ_T in

$$^1\text{P-567}^* + {}^3\Sigma_g^- \quad \rightarrow \quad {}^3\text{P-567}^* + {}^3\Sigma_g^- \tag{8}$$

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[2] We currently have no data concerning the nature of the chemical reaction between $^1\Delta_g$ and P-567. However, given the anticipated possible processes, allylic hydroperoxide, dioxetane or endoperoxide formation, all of them conjugation-breaking processes, it is extremely unlikely that a chemical product would absorb as far to the red as 480 nm, the monitoring wavelength in Fig. 6(2). Therefore, the estimated chemical reaction of ∼6% is not artificially low due to a balance between substrate and product absorptions at that wavelength.

$$^1\text{P-567}^* + {}^3\Sigma_g^- \quad \rightarrow \quad {}^3\text{P-567}^* + {}^1\Delta_g \tag{9}$$

aerated medium would indicate that this process is summarised by Eq. (8) rather than Eq. (9), a conclusion supported by the energetics of the situation. The *short wavelength* onset of the P-567 fluorescence (cf. Fig. 1) occurs at 505 nm corresponding to a maximum available donation energy of 56.8 kcal mol^{-1}. The triplet energy of 37.7 kcal mol^{-1} determined in this work thus gives a maximum $S_1 - T_1$ splitting of 19.1 kcal mol^{-1}, i.e. 3–4 kcal mol^{-1} less than the lowest electronic excitation

$$\phi_\Delta = \phi_T \times S_\Delta \tag{10}$$

requirement of the oxygen molecule. This also means that the relationship of Eq. (10) should hold where S_Δ is the fraction of oxygen quenchings of ^{3}P-567* which give $^1\Delta_g$ [20]. This parameter is clearly unity within experimental error. The fact that in benzene, some intersystem crossing takes place, that the triplet produces $^1\Delta_g$ with unit efficiency, and that the latter reacts with P-567 with a rate constant for chemical quenching of the order of 10^6 l mol^{-1} s^{-1} clearly demonstrates that the potential of this laser dye will be strongly dependant on the efficiency of exclusion of oxygen.[3]

Acknowledgements

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[3] Steady-state experiments [19] show that this undesirable process becomes more pronounced as more polar solvents are employed.