the second porphyrin ring that should be protonated in the acidic medium employed. It is conceivable that these protons, juxtaposed to the coordinated O_2, could prevent the premature dissociation of, as well as assist in proton transfer to, the partially reduced O_2 coordinated to the cobalt center in the second porphyrin ring. If such specific proton catalysis proves to be the case, it would suggest new directions for the design of catalysts for multielectron reductions.

Concluding Remarks

The anthracene-bridged cobalt diporphyrins examined in this study clearly provide four-electron pathways for the catalytic reduction of O_2 when adsorbed on graphite electrodes. This is true for both the dimetalated and monometalated derivatives. These molecules and their diphenylene-bridged analogues[7] represent the first effective macrocyclic metal complex electrocatalysts that do not depend upon the "four-atom separation" demonstrated to be essential in the case of the diamide-bridged catalysts of Collman et al.[1-6]

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Registry No. I, 94250-18-7; II, 94250-20-1; III, 87597-38-4; IV, 94250-19-8; O_2, 7782-44-7; H_2O_2, 7722-84-1.

Photoprocesses in Diphenylpolyenes. 3. Efficiency of Singlet Oxygen Generation from Oxygen Quenching of Polyene Singlets and Triplets[1,2]

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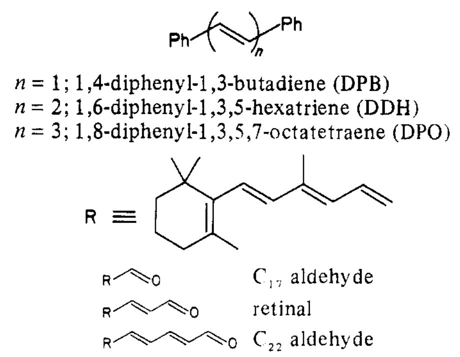
The efficiencies of singlet oxygen ($^1O_2$*) photogeneration from the oxygen quenching of the excited states (singlet/triplet) of retinal-related polyenals and diphenylpolyenes have been measured in cyclohexane and methanol by 337.1-nm laser flash photolysis. The $^1O_2$* yields are essentially quantitative with *all-trans*-retinal and its lower and higher homologues as triplet photosensitizers. For *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) and *all-trans*-1,8-diphenyl-1,3,5,7-octatetraene (DPO), both singlet and triplet quenching by oxygen contribute to the formation of $^1O_2$*; significant fractions (0.1–0.7) of the oxygen-induced intersystem crossing in these polyene systems take place without energy transfer to oxygen. The triplet-mediated $^1O_2$* yield obtained by steady-state photolysis of *all-trans*-1,4-diphenyl-1,3-butadiene (DPB) under energy-transfer sensitization by pyrene-1-aldehyde in O_2-saturated benzene is less than unity (0.7 ± 0.1), suggesting possible fractional quenching by oxygen at an orthogonal geometry of DPB triplet (responsible for "nonproduction" of $^1O_2$*).

Introduction

Quantitative aspects of singlet ($^1O_2$*, $^1\Delta_g$) production as a result of the quenching of singlet and triplet excited states by oxygen ($^3O_2$, $^3\Sigma_g^-$) constitute a subject of ongoing interest and controversy. The knowledge of the quantum efficiency of $^1O_2$* generation is important because of its frequent involvement as an oxidizing intermediate in sensitized photooxygenations of various organic and biological systems. Unless the singlet–triplet energy separation ($\Delta E_{S_1-T_1}$ or $\Delta E_{T_1-S_0}$) is smaller than the excitation energy (~8000 cm^{-1}) of oxygen, the oxygen quenching of electronically excited states, S_1 or T_1, generally occurs by energy transfer giving rise to assisted intersystem crossing ($T_1 \leftsquigarrow S_1$ or $S_0 \leftsquigarrow T_1$) as well as producing $^1O_2$* in high yields.[3] However, complications and variations are observed in many cases presumably because of charge transfer, spin exchange, or other interactions.[3-8]

In an earlier paper[2a] from this laboratory, we have presented kinetic data concerning the efficient quenching of the singlets and triplets of diphenylpolyenes by oxygen. However, the fate of the oxygen molecules participating in the quenching processes was not examined. In the work described in this paper, we have examined the efficacy of three all-trans diphenylpolyenes as well as three *all-trans*-retinal-related polyenals as photosensitizers for production of $^1O_2$*. The results are of interest not only because of the roles the polyenes play as light-harvesting agents in photobiological systems but also from the viewpoint that the geometric distortion of the polyenes in the excited states may favor oxygen quenching via spin exchange. It should be noted that the relatively high oxygen-quenching rate constant (8×10^9 M^{-1} s^{-1} in benzene)[9] for stilbene triplet has been associated[7] with spin-exchange interaction at the twisted geometry and the efficiency of $^1O_2$* generation as a result of this quenching has been shown[4a] to be small.

Chart I



n = 1; 1,4-diphenyl-1,3-butadiene (DPB)
n = 2; 1,6-diphenyl-1,3,5-hexatriene (DDH)
n = 3; 1,8-diphenyl-1,3,5,7-octatetraene (DPO)

C_{17} aldehyde
retinal
C_{22} aldehyde

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The structures of all-trans diphenylpolyenes and polyenals under examination and the acronyms used for them are shown in Chart I.

Experimental Section

The sources/syntheses and the methods of purification of the polyene systems under study are described elsewhere.[2a,10] Cyclohexane (MCB), methanol (Aldrich), and benzene (Aldrich) were of spectral grades. 1,3-Diphenylisobenzofuran (DPBF) and rubrene, both from Aldrich, were recrystallized from ethanol and benzene, respectively (under red light). For variable concentrations of oxygen, the solutions were saturated with $O_2 + N_2$ mixtures of known compositions (Linde). Pyrene-1-aldehyde (PA) from Pfaltz and Bauer was recrystallized thrice from aqueous ethanol.

For laser flash photolysis experiments, nitrogen laser pulses (337.1 nm, 8 ns, 2–3 mJ) from a Molectron UV-400 system were used for excitation. Details of the kinetic spectrophotometer are available in previous publications[2,11] from this laboratory. The laser flash photolysis experiments were performed in rectangular quartz cells of 1- or 2-mm path lengths and with optically flat surfaces across the analyzing light. In experiments where DPBF was used for monitoring ${}^1O_2{}^*$, suitable interference filters (ORIEL and Balzers) were placed in the path of the monitoring light to obtain a narrow spectral region at 400–440 nm (for registering DPBF consumption). The laser beam was generally defocused or its intensity attenuated by neutral density filters (Balzers) in order to ensure that the loss of DPBF in the course of the action of a given laser flash was ≤10% of the initial concentration used.

For steady-state photolysis, a medium-pressure Hg lamp (B&L SP-200) coupled with a monochromator (B&L 33-86-07) was employed as the source. The irradiation was carried out in 1 cm × 1 cm square cells (quartz) with optically flat surfaces. Rubrene was used as the trapping agent for ${}^1O_2{}^*$ in the course of steady-state photolysis, and its loss, monitored by absorbance change at 526 nm, was restricted to ≤10% (irradiation time 3–4 min).

Results

The various photoprocesses in the oxygen quenching of singlets and triplets under direct excitation are shown in the following scheme (S ≡ polyene substrate).

$$\text{excitation:}\quad {}^1S_0 \rightarrow {}^1S^* \tag{1}$$

$$\text{fluorescence:}\quad {}^1S^* \rightarrow {}^1S_0 + h\nu_F \tag{2}$$

$$\text{intersystem crossing:}\quad \rightarrow {}^3S^* \tag{3}$$

$$\text{internal conversion:}\quad \rightarrow {}^1S_0 \tag{4}$$

$$\text{singlet quenching by oxygen:}\quad {}^1S^* + {}^3O_2 \rightarrow {}^3S^* + {}^1O_2{}^* \tag{5}$$

$$\rightarrow {}^3S^* + {}^3O_2 \tag{6}$$

$$\rightarrow {}^1S_0 + {}^1O_2{}^* \tag{7}$$

$$\rightarrow {}^1S_0 + {}^3O_2 \tag{8}$$

$$\text{triplet decay:}\quad {}^3S^* \rightarrow {}^1S_0 \tag{9}$$

$$\text{triplet quenching by oxygen:}\quad {}^3S^* + {}^3O_2 \rightarrow {}^1S_0 + {}^3O_2 \tag{10}$$

$$\rightarrow {}^1S_0 + {}^1O_2{}^* \tag{11}$$

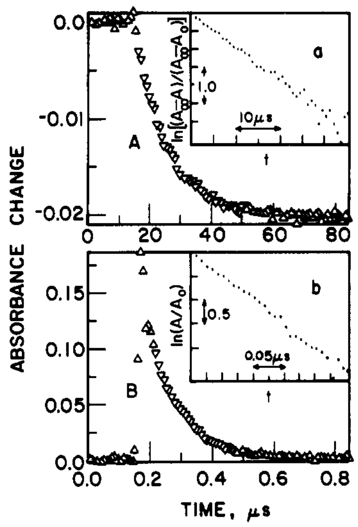

Figure 1. Experimental traces for (A) depletion of DPBF at 420 nm and (B) decay of DPO triplet at 437 nm, in a DPO solution in air-saturated cyclohexane containing 0.1 mM DPBF. The insets a and b show the first-order fits of the respective kinetic data.

In the presence of DPBF, the singlet oxygen produced from singlet/triplet quenching by oxygen undergoes deactivation and reaction with DPBF as follows:

$${}^1O_2{}^* \rightarrow {}^3O_2 \tag{12}$$

$${}^1O_2{}^* + \text{DPBF} \rightarrow \text{product} \tag{13}$$

At a given concentration of oxygen ($[O_2]$), the triplet yield (ϕ_{T,O_2}) and the singlet oxygen yield (ϕ_{Δ,O_2}) are given by relationships 14 and 15, respectively.

$$\phi_{T,O_2} = \frac{\phi_T^0 + \delta K_{SV}[O_2]}{1 + K_{SV}[O_2]} \tag{14}$$

$$\phi_{\Delta,O_2} = \frac{\phi_T^0\phi_\Delta^T + (\phi_\Delta^S + \delta\phi_\Delta^T)K_{SV}[O_2]}{1 + K_{SV}[O_2]} \tag{15}$$

where $\phi_T^0 = k_3\tau_F$ (i.e., intrinsic triplet yield) and $\tau_F^{-1} = \sum_{i=2}^{4} k_i$

$$K_{SV} = k_q^S\tau_F, \quad k_q^S = \sum_{i=5}^{8} k_i$$

$$\phi_\Delta^S = (k_5 + k_7)/k_q^S$$

$$\delta = (k_5 + k_6)/k_q^S$$

$$\phi_\Delta^T = k_{11}/k_q^T, \quad k_q^T = k_{10} + k_{11}$$

In obtaining eq 15, it has been assumed that the oxygen concentration is so high that the deactivation of the triplet is controlled entirely by the oxygen quenching (that is, $k_9 << k_q^T[O_2]$).

For retinal and its homologues, K_{SV}'s are negligible because of short singlet lifetimes (subnanosecond).[12-14] For these systems, at ordinary concentrations of oxygen, $\phi_T^0 = \phi_{T,O_2}$ and $\phi_{\Delta,O_2}/\phi_{T,O_2} = \phi_\Delta^T$. On the other hand, for DPH and DPO, K_{SV}'s are relatively large[2a] and ϕ_T^0's are negligible.[2a] For these systems, $\phi_{\Delta,O_2}/\phi_{T,O_2}$ is reduced to $(\phi_\Delta^S + \delta\phi_\Delta^T)/\delta$. If $\phi_\Delta^T = 1$ and the singlet quenching by oxygen is dominated by step 5 (particularly, $k_5 < k_6, k_7$), then $\phi_{\Delta,O_2}/\phi_{T,O_2}$ should approach a value of 2.

Measurement of $\phi_{\Delta,O_2}/\phi_{T,O_2}$ *in Air-Saturated Solutions.* For each of the polyene substrates under study (except DPB), the following experiment was carried out under 337.1-nm laser excitation using air-saturated solutions in cyclohexane and methanol. The solutions contained DPBF at 0.05–0.1 mM and the polyene substrates at such concentrations that the fractional absorbance due to the former at 337.1 nm corresponded to the absorption of

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TABLE I: Bimolecular Rate Constants, $k^{\mathrm{T}}_{\mathrm{q,O_2}}$, for the Quenching of Polyene Triplets by Oxygen and Efficiencies of Singlet Oxygen Formation Relative to Observed Polyene Triplet Yield in Air-Saturated Solutions

polyene (all-trans)	solvent	$k^{\mathrm{T}}_{\mathrm{q,O_2}}$,[a] 10^9 M^{-1} s^{-1}	δ	$\phi_{\Delta,O_2}/\phi_{T,O_2}$[b]
C_{17} aldehyde	cyclohexane	4.1		1.0
	MeOH	4.4		1.1
retinal	cyclohexane	3.9		1.1
	MeOH	4.5		1.1
C_{20} aldehyde	cyclohexane	4.4		1.4
DPH	cyclohexane	4.4[c]	0.7[c]	1.7
	MeOH	4.5[c]	0.5[c]	1.6
DPO	cyclohexane	4.8[c]	0.8[c]	1.9
	MeOH	5.1[c]	0.6[c]	1.4

[a] ±15%. [b] ±20%; in air-saturated solutions. [c] Taken from ref 2a.

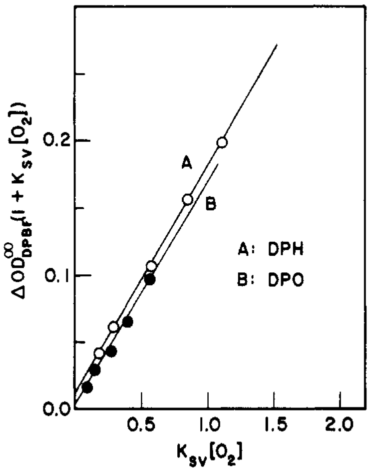

Figure 2. Plots of relative $^1O_2{}^*$ yields photosensitized by (A) DPH and (B) DPO in cyclohexane according to eq 15 (rearranged). K_{SV} data were taken from ref 2a, and $\Delta OD^{\infty}_{DPBF}$ data were obtained by 337.1-nm laser flash photolysis (see text).

≤10% of the laser photons. The decay traces of polyene T–T absorptions at the respective maxima (410–480 nm) were monitored over ~1 μs following the laser flash, and the end-of-pulse absorbance changes (ΔOD^0_T) were obtained by extrapolation. At the same time, the traces due to the depletion of DPBF were monitored at 400–440 nm on a time scale of 50–100 μs and the pseudo-first-order rate constants ($k^{\mathrm{obsd}}_{\mathrm{DPBF}}$) for the kinetics of depletion and the absorbance changes ($\Delta OD^{\infty}_{DPBF}$) at its completion were obtained for them. Figure 1 shows two experimental traces with DPO as the substrate. $\phi_{\Delta,O_2}/\phi_{T,O_2}$ was calculated from the following relationship

$$\frac{\phi_{\Delta,O_2}}{\phi_{T,O_2}} = \frac{\Delta OD^{\infty}_{DPBF}}{\Delta OD^0_T} \frac{\epsilon_T}{\epsilon_{DPBF}} \frac{k^{\mathrm{obsd}}_{\mathrm{DPBF}}}{k^{\mathrm{obsd}}_{\mathrm{DPBF}} - k_{12}} \qquad (16)$$

where ϵ_T and ϵ_{DPBF} represent the extinction coefficients of polyene triplet absorption and DPBF ground-state absorption at the respective monitoring wavelengths. A small correction was applied to the observed $\Delta OD^{\infty}_{DPBF}$ on the basis of blank experiments in which DPBF alone was used at the same concentrations as in the experiments above. The data concerning k_{12} and ϵ_T were available in the literature.[2a,8,15,16] The values obtained in this manner for $\phi_{\Delta,O_2}/\phi_{T,O_2}$ in air-saturated solutions as well as the rate constants for polyene triplet quenching by oxygen are given in Table I.

Relative Singlet Oxygen Yield as a Function of Oxygen Concentration for DPH and DPO. For DPH and DPO in cyclohexane, relative $^1O_2{}^*$ yields were measured at varying oxygen concentrations in terms of $\Delta OD^{\infty}_{DPBF}$ at a given DPBF concentration. Based on eq 15 (rearranged), the plot of $\Delta OD^{\infty}_{DPBF}(1 + K_{SV}[O_2])$ against $K_{SV}[O_2]$ should give a straight line with the slope-to-intercept ratio equal to $(\phi^S_\Delta + \delta\phi^T_\Delta)/(\phi^0_T\phi^T_\Delta)$. Figure 2 shows two such linear plots. Because of large uncertainties (ca. ±50%) in the small intercepts of these plots (owing to small ϕ^0_T for both DPH and DPO), estimates with high precision could not be obtained for $(\phi^S_\Delta + \delta\phi^T_\Delta)/\phi^T_\Delta$ from the slope-to-intercept ratios (1.0 ± 0.5 and 0.8 ± 0.4 for DPH and DPO, respectively).

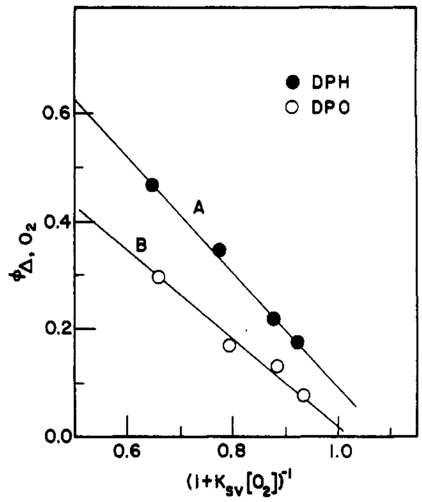

Figure 3. Plots of $^1O_2{}^*$ yields photosensitized by (A) DPH and (B) DPO in benzene according to eq 15 (rearranged). K_{SV} data were measured from fluorescence quenching by oxygen in benzene, and ϕ_{Δ,O_2} data were obtained by steady-state photolysis at 366 nm (see text).

The yields of $^1O_2{}^*$ photosensitized by DPH and DPO in benzene at varying oxygen concentrations were also determined under steady-state irradiation. Formation of $^1O_2{}^*$ sensitized by pyrene-1-aldehyde (PA) triplet in benzene was used for actinometry. PA in benzene is characterized by high intersystem crossing efficiency ($\phi^0_T = 0.57$)[17], short singlet lifetime ($\tau_F < 0.1$ ns),[17] and a ϕ^T_Δ value of unity.[8] Optically matched solutions of PA, DPH, and DPO, each containing 0.05 mM rubrene, were photolyzed at 366 nm in 1 cm × 1 cm cells for a given period of time. The decrease in absorbance at 526 nm due to loss of rubrene by peroxidation sensitized by the polyenes, normalized with respect to that by PA under identical conditions, was converted to ϕ_{Δ,O_2} by multiplying with $\phi^0_T\phi^T_\Delta$ of PA. Plots of ϕ_{Δ,O_2} against $(1 + K_{SV}[O_2])^{-1}$ are shown in Figure 3. Based on a rearranged form of eq 15, the intercepts of these plots are identifiable as $(\phi^S_\Delta + \delta\phi^T_\Delta)$. For DPH and DPO, we obtained values of 1.2 ± 0.3 and 0.9 ± 0.3, respectively, for $(\phi^S_\Delta + \delta\phi^T_\Delta)$.

Singlet Oxygen Yield from DPB Triplet Quenching under Steady-State Photolysis. These experiments were performed under steady-state excitation of PA acting as the sensitizer for DPB triplet formation in benzene; rubrene was employed for monitoring singlet oxygen. A solution of PA (absorbance = 0.8 in 1-cm cell at 410 nm) in oxygen-saturated benzene containing 0.07 M DPB and 0.056 mM rubrene was photolyzed at 405 nm for 3–4 min, and the resultant absorbance change at 526 nm due to rubrene consumption was compared with that observed under photolysis of PA + rubrene solution in the absence of DPB. Since the rate constants[17] for PA triplet quenching by DPB and O_2 are 7.6×10^9 and 1.9×10^9 M^{-1} s^{-1}, respectively, under the conditions of our experiments ($[O_2] \sim 0.01$ M and [DPB] = 0.07 M), PA triplets formed with a high yield ($\phi^0_T = 0.57$)[17] under direct excitation were quenched nearly entirely by DPB. From these experiments, a value of 0.7 ± 0.1 was obtained for the efficiency of $^1O_2{}^*$ production from DPB triplet quenching in O_2-saturated benzene. Note that in O_2-saturated benzene, DPB triplet decay was dominated by the quenching by O_2 ($\tau_T^{-1} << k^T_q[O_2]$).[18]

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Discussion

It is evident from the data in Table I that the efficiencies of $^1O_2^*$ production from the oxygen quenching of the triplets of retinal and its lower homologue (C_{17} aldehyde) are essentially unity ($\phi_\Delta^T = 1$) in both methanol and cyclohexane. These results indicate that orthogonal geometries at which oxygen quenching would occur by a spin-exchange mechanism[7] leading to nonproduction[4a] of $^1O_2^*$ are not important for the triplet states of these long-chain polyene systems. From $^1O_2^*$-mediated photooxidation of 2,5-dimethylfuran sensitized by retinal in methanol under steady-state irradiation, Delmelle[19] has estimated the quantum yield of $^1O_2^*$ production to be 0.096 which is close to the triplet yield measured for this polyenal in methanol (0.12).[15b] On the other hand, for retinol (vitamin A), the $^1O_2^*$ yield (ϕ_Δ^T) from triplet quenching by O_2 has been reported[20] to be quite low (0.25 ± 0.05); the low ϕ_Δ^T has been attributed[20] to charge-transfer (CT) interaction of the polyene triplet with oxygen. Interestingly, the rate constants for polyene triplet quenching by O_2 are all higher than $(1/9)k_{\text{diff}}$ (Table I) and give the impression that CT interaction or spin exchange at perpendicular geometries may be important in the quenching processes.

In the case of C_{22} aldehyde, the higher homologue of retinal, $\phi_{\Delta,O_2}/\phi_{T,O_2}$ in air-saturated cyclohexane is greater than unity (Table I). It is possible that the ϵ_T value (1.21×10^5 M^{-1} cm^{-1} at 470 nm in cyclohexane)[16] used for this polyenal is overestimated. Appreciable $^1O_2^*$ production via singlet quenching seems unlikely in an air-saturated solution in view of the short fluorescence lifetime ($\tau_F = 0.8$ ns in 3-methylpentane at 298 K).[12] We, however, note that a longer lived singlet species, distinct from the one responsible for fluorescence, has been implicated as the predominant precursor of triplet in the case of C_{22} aldehyde (based on quenching studies with alcohols and aromatic molecules).[21] The oxygen quenching of such a species may be nonnegligible and may contribute to $^1O_2^*$ photogeneration.

The $\phi_{\Delta,O_2}/\phi_{T,O_2}$ data for DPH and DPO (Table I) show clearly that the quenching of the singlets of these polyenes results in facile formation of $^1O_2^*$. The role of the singlet is specially important for DPH in cyclohexane because of the relatively long fluorescence lifetime ($\tau_F = 12.9$ ns under degassed conditions)[2a] which becomes 50% shorter upon air saturation. As discussed in the beginning of the Results section, $\phi_{\Delta,O_2}/\phi_{T,O_2}$ for the two diphenylpolyenes can be approximated to $(\phi_\Delta^S + \delta\phi_\Delta^T)/\delta$ on the basis of the fact that $\phi_T^0 \approx 0$. The data concerning δ, i.e., the fraction of singlets quenched by $^3O_2$ that give triplets, are available from our previous work[2a] and are included in Table I. Assuming $\phi_\Delta^T = 1$ in analogy to the behavior of retinal-related polyene triplets (vide supra) and using the values of δ (Table I), we obtain ϕ_Δ^S values of 0.5 and 0.3 for DPH in cyclohexane and methanol, respectively, and of 0.7 and 0.2 for DPO in cyclohexane and methanol, respectively. Coupled with the assumption that the photoprocess represented by eq 7 is spin forbidden and hence relatively unimportant, these data show that significant fractions (0.1–0.7) of oxygen-induced intersystem crossing (steps 5 and 6) occur without energy transfer to oxygen (process 6). According to the theoretical consideration by Stevens,[3h] the fractional ϕ_Δ^S values are explainable by a reencounter quenching of $^1O_2^*$ by $^3S^*$ following their formation by process 5.

DPB represents a transition between long-chain polyenes (DPH and DPO) and stilbene, the triplet of the latter being well-known[22] to exist in a perpendicular form. In an earlier paper,[18] we have suggested that the difference in the quenching behavior of DPB triplet relative to that of aromatic hydrocarbons of comparable triplet energies (e.g., anthracene) can be explained in terms of an equilibrium between planar ($^3t^*$) and perpendicular ($^3p^*$) forms of DPB triplet. With the assumption that the oxygen quenching of $^3t^*$ leads to the formation of $^1O_2^*$ while that of $^3p^*$ does not, one obtains the following expression for triplet-mediated $^1O_2^*$ yield (ϕ_Δ^T) at high $[O_2]$.

$$\phi_\Delta^T = \frac{k_{q,t}}{k_{q,\text{obsd}}(1 + K)} \tag{17}$$

K is the equilibrium constant for $^3t^* \rightleftarrows {}^3p^*$, $k_{q,t}$ is the individual rate constant for the oxygen quenching of the planar form, and $k_{q,\text{obsd}}$ is the observed, overall oxygen quenching rate constant (5.0×10^9 M^{-1} s^{-1} in benzene).[18] The departure of the observed ϕ_Δ^T (0.7 in benzene) from unity suggests that the model involving $^3t^* \rightleftarrows {}^3p^*$ is probably correct, although the value of K (~0.6) estimated[18] from azulene quenching data appears to be incompatible with the observed ϕ_Δ^T data. To be more specific, values of 0.6 for K and 0.7 for ϕ_Δ^T would lead to $k_{q,t} > k_{q,\text{obsd}}$ which seems unlikely because the quenching of the perpendicular form by spin-exchange interaction is expected to occur with a larger rate constant ($k_q^p > k_q^t$). It appears that $^1O_2^*$ production from the quenching of the orthogonal form of DPB triplet may not be totally inefficient.

Registry No. DPH, 17329-15-6; DPO, 22828-29-1; DPB, 538-81-8; O_2, 7782-44-7; C_{17} aldehyde, 6980-79-6; C_{22} aldehyde, 6985-27-9; retinal, 116-31-4.

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