

GENERATION OF $^1\text{O}_2$ FROM OXYGEN QUENCHING OF THE LOWEST EXCITED SINGLET AND TRIPLET STATES OF SOME AROMATIC COMPOUNDS[†]

H.-D. BRAUER, A. ACS, W. DREWS, R. GABRIEL, S. GHAENI and R. SCHMIDT

Institute for Physical and Theoretical Chemistry, University of Frankfurt, Robert Mayer Strasse 11, D-6000 Frankfurt am Main (F.R.G.)

(Received January 7, 1984)

Summary

Measurements of the overall quantum yield of the tetracene-, rubrene- and heterocoerdianthrone-sensitized photoperoxidation of 1,3-diphenylisobenzofuran and of the self-sensitized photoperoxidation of 9,10-dimethylanthracene, 9,10-diphenylanthracene, 1,4-dimethoxy-9,10-diphenylanthracene, benzodioxanthene, anthradichromene, dimethylhomocoerdianthrone and *meso*-diphenylhelianthrene as a function of dissolved oxygen are presented. The experimental results indicate that whenever the oxygen quenching of the S_1 state of the compounds investigated leads directly to the formation of the T_1 state molecular singlet oxygen in its $^1\Delta_g$ state is produced with an efficiency of about unity, if the S_1 - T_1 splitting exceeds the excitation energy of $\text{O}_2(^1\Delta_g)$ at 7880 cm^{-1} , *i.e.* the process $S_1 + ^3\text{O}_2 \rightarrow T_1 + ^3\text{O}_2$ is negligible compared with the energy transfer process $S_1 + ^3\text{O}_2 \rightarrow T_1 + \text{O}_2(^1\Delta_g)$. The results further imply that the S_1 state quenching of some aromatic compounds involves induced internal conversion. If the energy of the T_1 state exceeds the excitation energy of $\text{O}_2(^1\Delta_g)$ the oxygen quenching of T_1 occurs also only via the energy transfer mechanism $T_1 + ^3\text{O}_2 \rightarrow S_0 + \text{O}_2(^1\Delta_g)$.

1. Introduction

Measurements of the overall quantum yield Q_{PO} of the sensitized or self-sensitized photoperoxidation of a $^1\text{O}_2$ acceptor A as a function of the dissolved oxygen concentration can be analysed to identify the operative oxygen quenching process of the lowest excited singlet (S_1) and triplet (T_1) states of the sensitizer [1 - 12].

At least the following six processes must be considered for the oxygen quenching of the S_1 and T_1 states in non-polar solvents:

[†]Paper presented at the COSMO 84 Conference on Singlet Molecular Oxygen, Clearwater Beach, FL, U.S.A., January 4 - 7, 1984.



Only process (3) is spin forbidden, whereas all other processes are spin allowed and exothermic if both the singlet-triplet splitting ΔE_{ST} (process (1)) and the triplet energy E_T (process (5)) exceed the excitation energy of $O_2({}^1\Delta_g)$ at 7880 cm^{-1} . Under certain energy conditions 1O_2 may also be produced in its ${}^1\Sigma_g^+$ state (12815 cm^{-1}). However, its lifetime in liquid solutions is only about 10^{-11} s [13], so that it cannot participate in any chemical reaction.

In general the overall quantum yield Q_{PO} may be expressed as the product of the efficiency Φ_A of 1O_2 addition to an acceptor and the quantum yield Q_Δ of 1O_2 formation:

$$Q_{PO} = \Phi_A Q_\Delta \quad (I)$$

If only



are responsible for 1O_2 consumption, Φ_A is given by

$$\Phi_A = \frac{k_7^A[A]}{k_7^A[A] + k_8} = \frac{[A]}{[A] + \beta} \quad (II)$$

where $\beta = k_8/k_7^A$ is the reactivity parameter of the 1O_2 acceptor.

For many aromatic compounds laser photolysis experiments provide conclusive evidence that only T_1 formation accompanies S_1 quenching, *i.e.* processes (3) and (4) do not take place in S_1 quenching [14 - 17]. In this case

$$Q_\Delta = \frac{bQ_{isc}^0 + (a + b)(Q_{fl}^0/Q_{fl} - 1)}{Q_{fl}^0/Q_{fl}} \quad (III)$$

is derived, where Q_{isc}^0 is the quantum yield of the T_1 formation in the absence of oxygen, $a = k_1/(k_1 + k_2)$ and $b = k_5/(k_5 + k_6)$ are the efficiencies of 1O_2 generation in the corresponding channels of quenching and Q_{fl}^0/Q_{fl} is the ratio of the fluorescence quantum yields of the sensitizer in the absence and in the presence of oxygen respectively.

Combining eqns. (I) and (III)

$$Q_{PO} = \Phi_A \frac{bQ_{isc}^0 + (a+b)(Q_{fl}^0/Q_{fl} - 1)}{Q_{fl}^0/Q_{fl}} \quad (IV)$$

is obtained, which can be rearranged to

$$Q_{PO} \frac{Q_{fl}^0}{Q_{fl}} = \Phi_A b Q_{isc}^0 + \Phi_A (a+b) \left(\frac{Q_{fl}^0}{Q_{fl}} - 1 \right) \quad (V)$$

A linear plot of the data $Q_{PO}(Q_{fl}^0/Q_{fl})$ versus $Q_{fl}^0/Q_{fl} - 1$ provides the slope $\Phi_A(a+b)$, from which $a+b$ can be evaluated, if the value for Φ_A at the prevailing acceptor concentration is known.

The advantage of the use of eqn. (V) is that the slope can be determined rather exactly; however, the accuracy of the determination of β and therefore Φ_A is not high. The error in β determined by independent measurements lies in the range between 15% and 30%.

In principle, this disadvantage can be avoided by measurement of the photoperoxidation at acceptor concentrations sufficient to consume most of the 1O_2 produced by the sensitizer. In this case an error of about 50% in the β value of the acceptor would result in an error of only 5% - 15% in the calculated value of Φ_A . This can be done in a simple way by measurement of the sensitized photoperoxidation of an efficient 1O_2 acceptor such as 1,3-diphenylisobenzofuran (DIBF). However, it should be pointed out that such measurements should also be conducted at various oxygen concentrations and analysed according to eqn. (V).

In the present paper we report measurements of the photoperoxidation of DIBF sensitized by tetracene (TET), rubrene (RUB) and heterocoerdianthrone (HCD) and further of the self-sensitized photoperoxidation of 9,10-dimethylantracene (DMA), 9,10-diphenylantracene (DPA), 1,4-dimethoxy-9,10-diphenylantracene (DMDPA), benzo[1.2.3-kl;4.5.6-k'l']-dixanthene (BDX), anthra[1.9-bc;4.10-b'c']dichromene (ADC), dimethyl-homocoerdianthrone (HOCD) and also of *meso*-diphenylhelianthrene (MDH) as a function of oxygen concentration in various solvents.

2. Experimental section

2.1.1. Materials

TET was obtained from Aldrich Europe and was used without further purification. DIBF, DMA and DPA from Aldrich Europe were recrystallized twice from ethanol. DMDPA [18], RUB [19], HCD [20], HOCD [21], MDH [22, 23], BDX [24] and ADC [24] were prepared and purified following the methods described in the literature [18 - 24]. Toluene, benzene, CS_2 , acetic acid ethyl ester and diethyl ether (Merck Uvasol; spectroscopic grade) were used directly as obtained.

2.1.2. Apparatus

The apparatuses for determination of the photochemical quantum yields and for the fluorescence measurements have been described earlier [25].

Absorption spectra were recorded on a Zeiss DMR 10 or on a Perkin-Elmer PE 555 spectrophotometer.

2.2. Photoperoxidation studies

2.2.1. Sensitized photoperoxidation

Quantum yields of the sensitized photoperoxidation of DIBF solutions were determined as a function of dissolved oxygen in the range between 2×10^{-3} and 9×10^{-3} M. The oxygen concentration was varied in the following way: solutions containing DIBF and the sensitizer were deoxygenated to 10^{-4} Torr by five freeze-pump-thaw cycles and then saturated with air or pure oxygen at a known pressure. Before each measurement of the photoperoxidation the ratio Q_{fl}^0/Q_{fl} of the sensitizer was determined by comparing Q_{fl} with Q_{fl}^0 of a degassed solution of the same concentration of DIBF and sensitizer. The concentration of DIBF lay in the range $(1.5 - 3.5) \times 10^{-4}$ M. The concentrations of the sensitizers TET, RUB and HCD were kept at about 6×10^{-5} M, 2×10^{-5} M and 2×10^{-5} M respectively. Excitation wavelengths were set at 470 nm (TET), 546 nm (RUB) and 578 nm (HCD), where only the corresponding sensitizer absorbed. The photoperoxidation of DIBF was monitored spectrophotometrically at $\lambda = 410$ nm or $\lambda = 417$ nm. Bleaching levels of DIBF were in the vicinity of 10%. While TET, RUB and HCD themselves react with 1O_2 , they are considerably less reactive ($\beta(\text{TET}) = 2.4 \times 10^{-3}$ M in toluene [7], $\beta(\text{RUB}) = 9 \times 10^{-5}$ M in CS_2 [5] and $\beta(\text{HCD}) = 7 \times 10^{-4}$ M in toluene [6]) than DIBF in the corresponding solvents (Tables 1 and 2, see later) and photolysis produced negligible sensitizer bleaching.

2.2.2. Self-sensitized photoperoxidation

The measurements of the self-sensitized photoperoxidation of DMA, DPA, DMDPA, BDX, ADC, HOCD and MDH were performed in the way described in earlier papers [5, 6]. The concentrations of these compounds used for the measurements were as follows: [DMA] = 6×10^{-4} M in toluene, [DPA] = 2×10^{-4} M in toluene, [DMDPA] = 3.3×10^{-5} M in acetic acid ethyl ester, [DMDPA] = 1×10^{-4} M in diethyl ether and [BDX] = 2.8×10^{-4} M, [ADC] = 1×10^{-4} M and [HOCD] = 5×10^{-4} M in toluene. For MDH the measurements were carried out at [MDH] = 1×10^{-5} , 1×10^{-4} and 1×10^{-3} M in toluene. At 1×10^{-4} and 1×10^{-3} M the photoperoxidation of MDH was monitored spectrophotometrically by the increase in the MDH endoperoxide formed at $\lambda = 429$ nm [26]. For the photoperoxidation and the fluorescence quenching measurements the oxygen concentration was varied in the way described above.

3. Results

Figures 1 and 2 are typical plots of $Q_{PO}(DIBF)(Q_{fl}^0/Q_{fl})_S$ and $Q_{PO}(Q_{fl}^0/Q_{fl})$ versus $Q_{fl}^0/Q_{fl} - 1$ according to eqn. (V) of the RUB-sensitized photoperoxidation of DIBF and the self-sensitized photoperoxidation of DMA respectively. Tables 1 - 3 are summaries of the experimental data, where IN and SL are the intercepts and slopes of the straight lines according to eqn. (V). Q_{ic}^0 is the quantum yield of the singlet ground state formation by internal conversion in the absence of oxygen. In Table 4 the spectroscopic data of the compounds investigated are compiled.

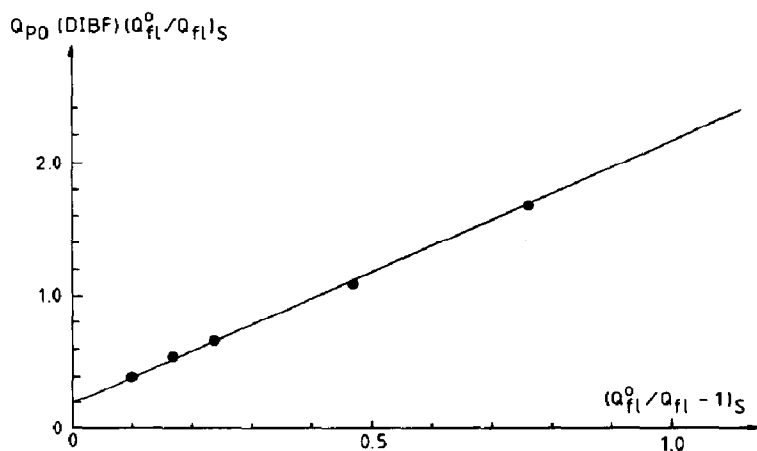


Fig. 1. Plot of $Q_{PO}(DIBF)(Q_{fl}^0/Q_{fl})_S$ vs. $(Q_{fl}^0/Q_{fl} - 1)_S$ for the rubrene-sensitized photoperoxidation of DIBF in CS_2 ($[DIBF] = 2 \times 10^{-4}$ M; $[RUB] = 2 \times 10^{-5}$ M; SL = 1.96; IN = 0.20; $a + b = 2.1 \pm 0.1$).

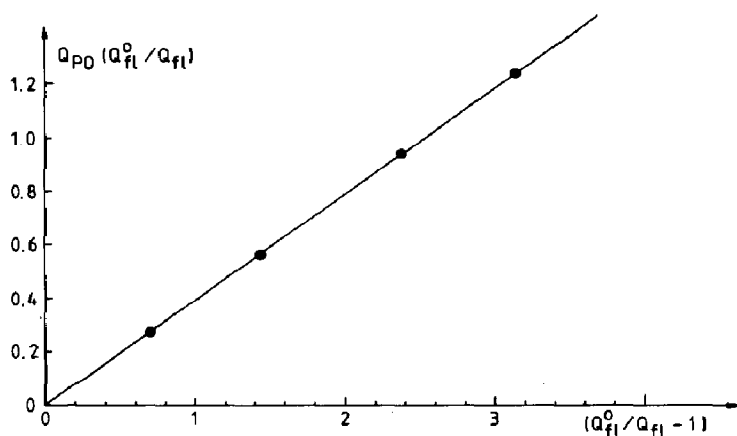


Fig. 2. Plot of $Q_{PO}(Q_{fl}^0/Q_{fl})$ vs. $Q_{fl}^0/Q_{fl} - 1$ for the self-sensitized photoperoxidation of DMA in toluene ($[DMA] = 6 \times 10^{-4}$ M; SL = 0.42; IN = 0.01; $\beta = (2.2 \pm 0.5) \times 10^{-3}$ M; $a + b = 2.0 \pm 0.3$).

TABLE 1
Photoperoxidation parameters

Sensitizer (S)	RUB	HCD	DMA	BDX
Acceptor (A)	DIBF	DIBF	DMA	BDX
Solvent	CS ₂	Benzene	Toluene	Toluene
β_A (M ⁻¹)	7.5×10^{-6}	6.0×10^{-5}	$(2.2 \pm 0.5) \times 10^{-3}$	$(5.1 \pm 0.8) \times 10^{-4}$
Φ_A	$0.95 \pm 0.02_5$ ^a	0.83 ± 0.06 ^a	0.21 ± 0.03	0.35 ± 0.03
$Q_{fl}(S)$	0.85 ± 0.04	0.93 ± 0.05	0.95 ± 0.05	0.97 ± 0.03
$K_{O_2}(S)$ ^b	169 ± 15	145 ± 15	435 ± 30	330 ± 20
$IN = \Phi_A b Q_{isc}^0(S)$	0.20 ± 0.02	0.020 ± 0.002	0.010 ± 0.001	0.030 ± 0.004
$SL = \Phi_A(a + b)(S)$	1.96 ± 0.07	1.58 ± 0.06	0.42 ± 0.01	0.66 ± 0.03
$Q_{isc}^0(S)$ ^c	0.21 ± 0.02	0.024 ± 0.004	0.05 ± 0.01	0.08 ± 0.03
$Q_{ic}^0(S)$ ^d	0	0	0	0
$(a + b)(S)$	2.1 ± 0.1	1.9 ± 0.2	2.0 ± 0.4	1.9 ± 0.3

^aThe error in Φ_A is estimated with an error in β_A of about 50%.

^bStern-Volmer constant for the oxygen quenching of the S₁ state of the sensitizer.

^cEstimated with $b = 1$.

^dEstimated from $Q_{fl}^0 + Q_{isc}^0 + Q_{ic}^0 = 1$.

TABLE 2
Photooxidation parameters

Sensitizer	TET	ADC	9,10-dibromoanthracene
Acceptor	DIBF	ADC	HOCD
Solvent	Toluene	Toluene	Toluene
β_A (M^{-1})	4×10^{-5}	$(9.5 \pm 2.0) \times 10^{-5}$	$(9.0 \pm 1.0) \times 10^{-5}$
Φ_A	0.79 ± 0.08^a	0.51 ± 0.05	0.85 ± 0.02
Q_{fl}^0 (S or A)	0.19 ± 0.01 (S)	0.39 ± 0.02 (S)	0.31 ± 0.02 (A)
K_{O_2} (S or A) ^b	130 ± 10 (S)	160 ± 10 (S)	150 ± 15 (A)
$IN = \Phi_A b Q_{isc}^0$ (S or A)	0.46 ± 0.02 (S)	0.005 ± 0.001 (S)	—(A)
$SL = \Phi_A(a + b)$ (S or A)	0.91 ± 0.0 (S)	0.39 ± 0.03 (S)	—(A)
Q_{isc}^0 (S or A) ^c	0.61 ± 0.10 (S)	0.010 ± 0.003 (S)	—(A)
Q_{ic}^0 (S or A) ^d	≈ 0.19 (S)	≈ 0.60	—(A)
$(a + b)$ (S)	1.2 ± 0.2 (S)	0.8 ± 0.1 (S)	0(A)

^aThe error in Φ_A is estimated with an error in β_A of about 50%.

^bStern-Volmer constant for the oxygen quenching of the S_1 state of the sensitizer or acceptor.

^cEstimated with $b = 1$.

^dEstimated from $Q_{fl}^0 + Q_{isc}^0 + Q_{ic}^0 = 1$.

TABLE 3
Photoperoxidation parameters

Sensitizer or acceptor	DPA	DMDPA	DMDPA	MDH
Solvent	Toluene	Acetic acid ethyl ester	Diethyl ether	Toluene
$\beta_A (M^{-1})$	$(3.1 \pm 0.3) \times 10^{-2}$ ^a	$(9.3 \pm 1.3) \times 10^{-5}$	$(2.4 \pm 0.5) \times 10^{-4}$	$(5.5 \pm 0.8) \times 10^{-6}$ ^b
Φ_A	$(7.7 \pm 0.8) \times 10^{-3}$ ^a	0.26 ± 0.02	0.29 ± 0.03	≈ 1
Q_{fl}^0	0.90 ± 0.05	0.71 ± 0.05	0.83 ± 0.05	0.21 ± 0.01
K_{O_2} ^c	190 ± 12	810 ± 30	1070 ± 50	89 ± 9
$IN = \Phi_A b Q_{isc}^0$	$(6.0 \pm 0.5) \times 10^{-4}$	0.022 ± 0.005	≈ 0	0.16 ± 0.02
$SL = \Phi_A (a + b)$	$(6.3 \pm 0.3) \times 10^{-3}$	0.18 ± 0.01	0.20 ± 0.01	0.35 ± 0.03 ₅
Q_{isc}^0 ^d	0.08 ± 0.03	0.08 ± 0.02	≈ 0	0.16 ± 0.02
Q_{ic}^0 ^e	≈ 0	≈ 0.20	≈ 0.17	≈ 0.63
$a + b$	0.8 ± 0.1	0.69 ± 0.10	0.69 ± 0.10	0.35 ± 0.03 ₅

^aFrom refs. 27 and 28.

^bFrom ref. 23.

^cStern-Volmer constant for the oxygen quenching of the S_1 state of the sensitizer.

^dEstimated with $b = 1$.

^eEstimated from $Q_{fl}^0 + Q_{isc}^0 + Q_{ic}^0 = 1$.

TABLE 4
Spectroscopic parameters of the sensitizer or acceptor

Sensitizer or acceptor	E_{S_1} (cm^{-1})	$E_{S_1} - E_{T_n}$ (cm^{-1})	E_{T_n} (cm^{-1})
RUB (S)	18400	9400 ^b	9000 ^b
HCD (S)	16900	≈ 8400 ^c	≈ 8500 ^c
DMA (S)	25120	11120 ^d	14000 ^d
BDX (S)	18200	≈ 8400 ^c	≈ 9800 ^c
TET (S)	21200	490 ^{d,e}	10530 ^d
ADC (S)	16600	≈ 7000 ^c	≈ 9600 ^c
HOCD (A)	14700	< 7800 ^{c,f}	< 7880 ^{c,f}
DPA (S)	25190	11190 ^d	14000 ^d
DMDPA (S)	22400	≈ 8400 ^g	≈ 14000 ^g
MDH (S)	16800	≈ 2800 ^{c,e}	≈ 14000 ^{c,e}

^a $n = 1$, unless otherwise specified.

^bFrom ref. 29.

^cEstimated from measurements of the oxygen quenching of the fluorescence by iodopropane [30].

^dFrom ref. 31.

^e $n = 2$.

^fFrom measurement of the photoperoxidation of HOCD.

^gAssumed that substituents in the 1,4 position of anthracene do not influence noticeably the energy of the T_1 states.

4. Discussion

It can be noted from Table 1 that the sum of the efficiencies $a + b$ of $^1\text{O}_2$ formation for RUB, HCD, DMA and BDX amounts to 2, indicating that the oxygen quenching of both the S_1 and the T_1 states of these compounds occurs only via the energy transfer mechanisms (1) and (5). Reactions (2) and (6) do not take place. The results for RUB, HCD and DMA are in excellent agreement with results of previous measurements [5 - 7, 32, 33]. Furthermore from the values of $a + b = 2$ it can be deduced that in these four compounds the S_1-T_1 energy gap and the T_1-S_0 energy gap are both equal to or larger than the excitation energy of $\text{O}_2(^1\Delta_g)$ at 7880 cm^{-1} . This is in agreement with the values for these energy gaps given in Table 4, which are estimated from other results.

For TET and ADC (Table 2) the estimated values for $a + b$ amount to 1.2 ± 0.2 and 0.8 ± 0.1 respectively. Taking into account the values for the S_1-T_n splitting and the energies of the T_1 state of these compounds (Table 4) it can be concluded that the oxygen quenching of the S_1 state leading to the triplet manifold formation occurs via process (2) and that the energy transfer from these compounds to oxygen takes place only from the T_1 state (process (5)). For TET our result confirms the results of Stevens and Ors [7] and Merkel and Herkstroeter [8].

For HOCD (Table 2) it was found that this compound is a very reactive $^1\text{O}_2$ acceptor, but it cannot produce $^1\text{O}_2$ by itself [34]. This indicates that for this compound the S_1-T_1 splitting and the energy of the T_1 state are both smaller than the excitation energy of $^1\text{O}_2$ in its $^1\Delta_g$ state (Table 4).

The measurements of the self-sensitized photoperoxidation of DPA, DMDPA and MDH led to remarkable results (Table 3). For DPA and DMDPA it can be assumed that the S_1-T_1 splitting and the energy of the T_1 state are both larger than the excitation energy of $^1\text{O}_2$ and that in both compounds the T_2 state is located above the S_1 state (Table 4). Therefore values of about 2 are expected to be found for $a + b$ in analogy with DMA. However, $a + b$ was found to be only 0.8 for DPA in toluene and 0.7 for DMDPA in acetic acid ethyl ester and diethyl ether.

For MDH the rate of quenching of the MDH fluorescence by iodo-propane is consistent with a splitting between the S_1 state and the nearest lower triplet state (probably the T_2 state) of about 2800 cm^{-1} which would locate the T_2 state at about $14\,000\text{ cm}^{-1}$. Furthermore, from the measurements of the overall quantum yield Q_{PO} of air-saturated MDH solutions as a function of temperature in the range between $+20$ and $-20\text{ }^\circ\text{C}$ which show that Q_{PO} is independent of temperature [35], it can be concluded that the energy of the triplet state of MDH being quenched by oxygen is equal to or larger than the excitation energy of $\text{O}_2(^1\Delta_g)$. Consequently, a value of about 1 for $a + b$ is expected to be found as for TET, but the value determined only amounts to 0.35. Initially we had no explanation for these results.

However, recently Darmanyan [36] could show by laser experiments that for DPA the oxygen quenching of the S_1 state leads not only to the formation of the T_1 state but also to the formation of the singlet ground state.

In this case eqn. (V), which we have used until now, is not correct. If processes (1), (2) and (4) are responsible for the oxygen quenching of the S_1 state, eqn. (V) assumes the form

$$Q_{PO} \frac{Q_{fl}^0}{Q_{fl}} = \Phi_A b Q_{isc}^0 + \Phi_A (a + b) d \left(\frac{Q_{fl}^0}{Q_{fl}} - 1 \right) \quad (VI)$$

where $d = (k_1 + k_2)/(k_1 + k_2 + k_4)$ is the efficiency of the T_1 state formation accompanying the oxygen quenching of the S_1 state [27, 28].

Darmanyan could show that $d = 0.33$ and therefore from the experimental value for $(a + b)d = 0.8$ a value for $a + b = 2.4 \pm 0.4$ is obtained. This value indicates that whenever the oxygen quenching of the S_1 state of DPA results in the formation of the T_1 state, 1O_2 is produced by process (1) and that the oxygen quenching of the T_1 state occurs only via the energy transfer process (5).

Darmanyan assumes that the internal conversion for DPA involves formation of sterically hindered conformers as the phenyl rings which are turned by 66° with respect to the anthracene frame [37] turn by 48° around the C—C bond. This assumption agrees with the observations that the quantum yield Q_{ic}^0 depends strongly on temperature and viscosity of the solution [36].

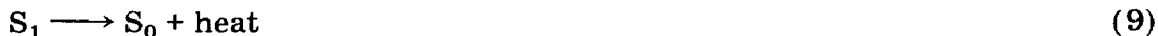
At present we do not know whether DMDPA and MDH show the same or similar behaviour with respect to the oxygen quenching of the S_1 state as does DPA. However, if it is assumed that this is the case and if it is further assumed that the efficiency d is also 0.33 for DMDPA and MDH, then from the respective values of the slopes $(a + b)d$, i.e. $(a + b)d = 0.69 \pm 0.1$ for DMDPA in acetic acid ethyl ester, $(a + b)d = 0.69 \pm 0.10$ for DMDPA in diethyl ether and $(a + b)d = 0.35 \pm 0.05$ for MDH in toluene, values of about 2 for DMDPA and a value of about 1 for MDH are obtained. This is very surprising; nevertheless, these results are in satisfactory agreement with the expectations described above.

Since these compounds like DPA possess two phenyl groups these results could imply that whenever two slightly revolving phenyl groups are present in a given compound of the type investigated here, the oxygen quenching of the S_1 state leads with an efficiency of only 30% to the nearest lower triplet state. To prove this hypothesis we intend to prepare and to investigate more diphenyl-substituted compounds of similar structure.

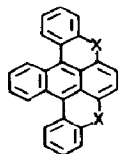
From the values of IN (Tables 1 - 3) the quantum yield Q_{isc}^0 of the intersystem crossing can be estimated. It should be noted that the conventional approximation often used for aromatic hydrocarbons $Q_{fl}^0 + Q_{isc}^0 = 1$ holds for RUB, HCD, DMA and BDX, i.e. sensitizers of high fluorescence yields. DPA and DMDPA are also sensitizers of high fluorescence yields,

but it seems to be likely that $Q_{fl}^0 + Q_{isc}^0 \neq 1$. For DPA in toluene it was found that $Q_{ic}^0 \approx 0$, but in this respect it must be conceded that only the measurements of photoperoxidation lead to this conclusion as has been discussed in ref. 27. For DMDPA in acetic acid ethyl ester and diethyl ether Q_{ic}^0 was estimated to be 0.20 and 0.17 respectively.

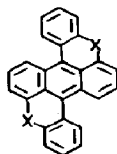
Finally, for the sensitizers of low fluorescence yields investigated, TET, ADC and MDH, apparently the internal conversion process



plays an important role. The estimated values for Q_{ic}^0 are 0.19 (TET), 0.60 (ADC) and 0.63 (MDH). Within this context it is interesting to note that for MDH the internal conversion process (9) can take place via the mechanism discussed for DPA, since MDH also possesses two phenyl groups. This possibility can be excluded for TET and also for ADC. ADC, HOCD, BDX and HCD can be considered as derivatives of DPA in which the two phenyl groups are linked by oxygen or keto bridges with the anthracene frame in the 1,4 position (ADC, HOCD) and 1,5 position (BDX, HCD) [24]:



ADC: X = O
HOCD: X = CO



BDX: X = O
HCD: X = CO

Therefore, the formation of sterically hindered conformers due to turning of the two phenyl groups of DPA cannot take place in ADC, HOCD, BDX and HCD. The observed internal conversion process (9) for ADC must occur via another mechanism.

Comparing the photophysical and photochemical behaviour of HCD and BDX on the one hand and HOCD and ADC on the other hand it is very astonishing that the different position of the linked keto or oxygen bridges provides so drastic a change. HCD and BDX are sensitizers of high fluorescence yields and are moderately reactive towards 1O_2 . In contrast, HOCD and ADC are compounds with "low" fluorescence quantum yields, but are a factor of about 10 more reactive towards 1O_2 . Probably the difference in the fluorescence quantum yields is due to the fact that HCD and BDX can be derived from perylene, whereas HOCD and ADC can be derived from pyrene [38].

In summarizing our results it can be said that if our assumptions hold true the compounds investigated can be classified into two groups with respect to oxygen quenching of the S_1 state.

(I) In the first group of compounds the oxygen quenching of the S_1 state results exclusively in the formation of the nearest lower triplet state (T_2 or T_1).

(II) In the second group of compounds the oxygen quenching of the S_1 state may lead either to the formation of the nearest lower triplet state (T_2 or T_1) or to the formation of the singlet ground state.

Within both groups it is possible to distinguish the two types of compounds further with respect to 1O_2 generation. Thus the following subdivision is useful.

(I.1) Each molecule being quenched by oxygen generates two molecules of 1O_2 . This is the case for RUB, HCD, MDA and BDX. The oxygen quenching of the S_1 and T_1 states of these compounds occurs only via processes (1) and (5).

(I.2) Each molecule in the S_1 state being quenched by oxygen generates only one molecule of 1O_2 . This is the case for TET and ADC. The oxygen quenching of the S_1 state occurs via process (2) and the oxygen quenching of the T_1 state takes place via process (5).

(II.1) Each molecule in the S_1 state which, on oxygen quenching, passes to the T_1 state generates two molecules of 1O_2 . This is the case for DPA and probably for DMDPA. In these compounds the oxygen quenching of the S_1 and T_1 states occurs via processes (1), (4) and (5).

(II.2) Each molecule in the S_1 state which, on oxygen quenching, passes to the nearest lower triplet state generates only one molecule of 1O_2 . Probably this is the case for MDH, where processes (2), (4) and (5) take place.

Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work.

References

- 1 B. Stevens and B. E. Algar, *J. Phys. Chem.*, **72** (1968) 3468.
- 2 B. Stevens and B. E. Algar, *J. Phys. Chem.*, **73** (1969) 1711.
- 3 B. Stevens and B. E. Algar, *Ann. N.Y. Acad. Sci.*, **171** (1970) 50.
- 4 B. Stevens and L. E. Mills, *Chem. Phys. Lett.*, **15** (1972) 381.
- 5 H.-D. Brauer and H. Wagener, *Ber. Bunsenges. Phys. Chem.*, **79** (1975) 597.
- 6 H. Wagener and H.-D. Brauer, *Mol. Photochem.*, **7** (1976) 441.
- 7 B. Stevens and J. A. Ors, *J. Phys. Chem.*, **80** (1976) 2164.
- 8 P. B. Merkel and W. G. Herkstroeter, *Chem. Phys. Lett.*, **53** (1978) 350.
- 9 K. C. Wu and A. M. Trozollo, *J. Phys. Chem.*, **83** (1979) 2823.
- 10 K. C. Wu and A. M. Trozollo, *J. Phys. Chem.*, **83** (1979) 3180.
- 11 B. Stevens, K. L. Marsh and J. A. Barltrop, *J. Phys. Chem.*, **85** (1981) 3079.
- 12 K. L. Marsh and B. Stevens, *J. Phys. Chem.*, **87** (1983) 1765.
- 13 B. P. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, **94** (1972) 7244.
- 14 G. Porter and M. R. Topp, *Proc. R. Soc. London, Ser. A*, **315** (1970) 163.
- 15 J. T. Richards, G. West and J. K. Thomas, *J. Phys. Chem.*, **74** (1970) 4137.
- 16 C. R. Goldschmidt, P. Potashnik and M. Ottolenghi, *J. Phys. Chem.*, **75** (1971) 1025.

- 17 R. Potashnik, C. R. Goldschmidt and M. Ottolenghi, *Chem. Phys. Lett.*, 9 (1971) 424.
- 18 Ch. Dufraisse and L. Velluz, *Bull. Soc. Chim. Fr.*, 9 (1942) 171.
- 19 W. Koblitz and W. Wittmeyer, *Ber. Dtsch. Chem. Ges.*, 69 (1936) 1806.
- 20 R. Scholl, H. K. Meyer and W. Winkler, *Justus Liebigs Ann. Chem.*, 494 (1932) 201.
- 21 R. Scholl and H. K. Meyer, *Justus Liebigs Ann. Chem.*, 512 (1934) 112.
- 22 G. Sauvage, *Ann. Chim. (Paris)*, 12 (1947) 844.
- 23 A. Acs, R. Schmidt and H.-D. Brauer, *Photochem. Photobiol.*, 38 (1983) 527.
- 24 R. Schmidt, W. Drews and H.-D. Brauer, *J. Photochem.*, 18 (1982) 365.
- 25 W. Drews, R. Schmidt and H.-D. Brauer, *J. Photochem.*, 6 (1977) 391.
- 26 H.-D. Brauer, R. Schmidt, G. Gauglitz and S. Hubig, *Photochem. Photobiol.*, 37 (1983) 595.
- 27 W. Drews, R. Schmidt and H.-D. Brauer, *Chem. Phys. Lett.*, 100 (1983) 466.
- 28 H.-D. Brauer and R. Schmidt, *Chem. Phys. Lett.*, 100 (1983) 470.
- 29 W. G. Herkstroeter and B. P. Merkel, *J. Photochem.*, 16 (1981) 331.
- 30 H. Dreeskamp, E. Koch and M. Zander, *Ber. Bunsenges. Phys. Chem.*, 78 (1974) 1328.
- 31 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, New York, 1970.
- 32 G. P. Gurinovich and K. I. Salokhiddinov, *Chem. Phys. Lett.*, 85 (1982) 9.
- 33 A. P. Darmanyan, *Chem. Phys. Lett.*, 86 (1982) 405.
- 34 R. Schmidt, W. Drews and H.-D. Brauer, *J. Phys. Chem.*, 86 (1982) 4909.
- 35 H.-D. Brauer, unpublished results, 1980.
- 36 A. P. Darmanyan, *Chem. Phys. Lett.*, 91 (1982) 396.
- 37 T. D. S. Hamilton, *Photochem. Photobiol.*, 3 (1964) 303.
- 38 E. Clar, *Polycyclic Hydrocarbons*, Vol. 2, Academic Press, New York, 1964.